

Chapter 7

Flowback and Produced Water

7. Flowback and Produced Water

7.1. Introduction

Water is a byproduct of oil and gas production. After hydraulic fracturing is completed, either in its entirety or for a specified stage, the operator reduces the injection pressure. Water is allowed to flow back from the well to prepare for oil or gas production. This return-flow water may contain chemicals injected as part of the hydraulic fracturing fluid, chemicals characteristic of the formation, hydrocarbons, and in-situ reaction and degradation products. Initially this water, called flowback, is mostly fracturing fluid, but as time goes on, it becomes more similar to the formation water. For formations containing saline water (brine), the salinity of the water increases as time passes, marking the increased contact time with the formation and in some cases the flow of formation water itself. This later stage water is called produced water, a term which can also refer to flowback and produced water collectively.

Flowback and produced water are stored and accumulated at the surface for eventual reuse or disposal. Typical storage facilities include open air impoundments and closed containers such as those shown in Figure 1-1. Produced water is collected and may be taken to disposal wells, recyclers, wastewater treatment plants, or in some cases the water may be left in pits to evaporate or infiltrate. Flowback and produced water leaks can occur on the well pad as a result of human error, failure of container integrity, equipment failure, communication between wells, pipeline leaks, and blowouts.¹ Above-ground piping systems can connect multiple well pads to impoundments, and piping or impoundments may leak. Much produced water is transported by truck, and pad incidents leading to spills of produced water can occur when trucks are filled. On-road accidents are also possible, some of which could release produced water loads to the environment.

Impacts to drinking water resources can occur if spilled flowback or produced water enters surface water bodies or aquifers. Environmental transport of chemical constituents depends on the characteristics of the spill, the fluid (e.g., density, as for highly saline water), the chemicals, and the environment. Attenuation processes (e.g., dilution, biodegradation of organics) in surface water and aquifers tend to reduce concentrations.

We begin this chapter with a review of definitions for flowback and produced water. We then discuss typical volumes of flowback and produced water on a per-well basis. This information is aggregated to the state and basin level in Chapter 8. The characteristics of hydraulically fractured shale, tight, and coalbed methane (CBM) formations are described. Spatial and temporal trends on composition of produced water are illustrated with examples from the literature and data compiled for this report. The processes controlling the chemical composition of produced water are described in Appendix E. The potential for impacts on drinking water resources of flowback and produced water are described based on reported spill incidents, contaminant transport principles, and field study examples. The chapter concludes with a discussion of uncertainties and knowledge

¹ For discussion of well communication, see Chapter 6.

gaps, factors that influence the severity of impacts, and a synthesis based on the EPA research questions.

7.1.1. Definitions

Multiple definitions exist for the terms flowback and produced water. These differing definitions indicate challenges in determining the distinctions between the two terms or indicate that different usage of the terms routinely occurs among various industry, private, and public groups. However, the majority of produced water definitions are fundamentally similar. The following definition is used in this report: water that flows from oil or gas wells.

This definition is similar to the definition used by the American Petroleum Institute (API): “Produced water is any of the many types of water produced from oil and gas wells” ([API, 2010b](#)); the definition used by the Department of Energy (DOE): “Produced water is water trapped in underground formations that is brought to the surface along with oil or gas” ([DOE, 2004](#)), and a similar definition used by the American Water Works Association (AWWA): “Produced water is the combination of flowback and formation water that returns to the surface along with the oil and natural gas” ([AWWA, 2013](#)). Produced water can variously refer to formation water, a mixture of spent hydraulic fracturing fluid and formation water or returned hydraulic fracturing fluid. Thus the term produced water is used when a distinction between fracturing fluid and formation water is not necessary.

In general, the term flowback refers either to fluids predominantly containing hydraulic fracturing fluid that returns to the surface or to a process used to prepare the well for production. Because formation water can contact and mix with injection fluids, the distinction between returning hydraulic fracturing fluid and formation water is not clear. In the early stages of operation, however, a higher concentration of chemical additives is expected and later, water that is typical of the formation ([Stewart, 2013a](#)). In most cases, a precise distinction between these waters is not determined during operations.

Various definitions have been used for the term flowback. The American Petroleum Institute defined flowback as “the fracture fluids that return to the surface after a hydraulic fracture is completed,” ([API, 2010b](#)) and the American Water Works Association used “fracturing fluids that return to the surface through the wellbore after hydraulic fracturing is complete” ([AWWA, 2013](#)). Other definitions include production of hydrocarbons from the well ([Barbot et al., 2013](#); [U.S. EPA, 2012f](#)), or a time period ([USGS, 2014f](#); [Haluszczak et al., 2013](#); [Warner et al., 2013b](#); [Hayes and Severin, 2012a](#); [Hayes, 2009](#)). As mentioned above, flowback can also be defined as a process used to stimulate the well for production by allowing excess liquids and proppant to return to the surface. Because we use existing literature in our review, we do not introduce a preferred definition of flowback, but rather we mention the assumptions used by the author(s) we discuss.

7.1. Volume of Hydraulic Fracturing Flowback and Produced Water

The characteristics and volume of flowback and produced water vary by well, formation, and time. This section presents information on flowback and produced water volume over various time scales, and where possible, on a per-well and per-formation basis.

The amount of flowback from a well varies and depends on several types of factors, including: production, formation, and operational. Production factors include the amount of fluid injected, type of hydrocarbon produced (gas or liquid), and location within the formation. Formation factors include the formation pressure, interaction between the formation and injected fluid (capillary forces) and reactions within the reservoir. Operational factors include loss of mechanical integrity and subsurface communication between wells ([U.S. GAO, 2012](#); [Byrnes, 2011](#); [DOE, 2011a](#); [GWPC and ALL Consulting, 2009](#); [Reynolds and Kiker, 2003](#)). The latter two factors might be indicated by an unexpected increase in water production ([Reynolds and Kiker, 2003](#)).

The processes that allow gas and liquids to flow are related to the conditions along the faces of fractures. [Byrnes \(2011\)](#) conceptualized fluid flow across the fracture face as being composed of three phases. The first is characterized by forced imbibition of fluid into the reservoir and occurs during and immediately following fracture stimulation. Second is an unforced imbibition following stimulation where the fluid redistributes within the reservoir rock, due to capillary forces, when the well is shut-in. The last phase consists of flow out of the formation when the well is opened and pressure reduced in the borehole and fractures. The purpose of this phase is to recover as much of the injected fluid as possible ([Byrnes, 2011](#)) in order to reduce high water saturations at the fracture face and eventually allow higher gas flow rates. The length of the last phase and consequently, the amount of water removed depends on factors such as the amount of injected fluid, the permeability and effective permeability of the reservoir, capillary pressure properties of the reservoir rock, the pressure near the fracture faces, and whether the well is flowing or shut in.¹ The well can be shut in for varying time periods depending on operator scheduling, surface facility construction or hookup, or other reasons.

7.1.1. Flowback of Injected Hydraulic Fracturing Fluid

Generally, the fluid that initially returns to the surface has been attributed to a mixture of the injected fracturing fluid, its transformation products, and the natural formation water. In some cases, as shown below, the amount of flowback is greater than the amount of injected hydraulic fracturing fluid and the additional water comes from the formation ([Nicot et al., 2014](#)) or an adjacent formation ([Arkadaskiy and Rostron, 2013a](#)). Several authors used geochemical analyses to postulate mixing between formation water and injected fluid in the Marcellus Shale ([Engle and Rowan, 2014](#); [Barbot et al., 2013](#); [Haluszczak et al., 2013](#)); Rowan et al., 2015). These possible explanations are summarized in a following section (see Section 7.6.4). Salinity increases in flowback from highly saline formations, so it is not possible to specify precisely the amount of injected fluids that return in the flowback ([GWPC and ALL Consulting, 2009](#)). Rather, such estimates relate the amount of produced water measured at a given time after fracturing as a percentage of the total amount of injected fluid.

Estimates vary but in composite indicate on average that between 5% and 75% (see Table 7-1, Table 7-2, and Table 7-3) of the volume of injected fracturing fluid may flow back to the surface

¹ When multiple fluids (water, oil, gas) occupy portions of the pore space, the permeability to each fluid depends on the fraction of the pore space occupied by the fluid and the fluid's properties. As defined by [Dake \(1978\)](#), when this effective permeability is normalized by the absolute permeability, the resulting relationship is known as the relative permeability.

after hydraulic fracturing is complete ([U.S. EPA, 2015g](#); [Vengosh et al., 2014](#); [Mantell, 2013b](#); [Vidic et al., 2013](#); [Minnich, 2011](#); [Xu et al., 2011](#)). These data (see Table 7-1) illustrate that the formations differ in their water requirements for hydraulic fracturing and generation of produced water over the short term.¹ Low percentages of flowback are typical, as is the decrease of flowback volume with time as the wells enter the production phase ([Gregory et al., 2011](#); [McElreath, 2011](#); [GWPC and ALL Consulting, 2009](#)). Some formations produce higher volumes, as noted for the Barnett Shale in Texas ([Nicot et al., 2014](#)) and discussed below.

Table 7-1. Data from one company’s operations indicating approximate total water use and approximate produced water volumes within 10 days after completion of wells ([Mantell, 2013b](#)).

Formation	Approx. total average water use per well (million gal)	Produced water within the first 10 days after completion		Produced water as a percentage of average water use per well	
		Low estimate (million gal)	High or only estimate (million gal)	Low estimate (% of total water use)	High or only estimate (% of total water use)
Gas shale plays (primarily dry gas)					
Barnett ^a	3.4	0.3	1.0	9	29
Marcellus ^a	4.5	0.3	1.0	7	22
Haynesville	5.4	--	0.25	--	5
Liquid plays (gas, oil, condensate)					
Mississippi Lime	2.1	--	1.0	--	48
Cleveland/Tonkaw	2.7	0.3	1.0	11	37
Niobrara	3.7	0.3	1.0	8	27
Utica	3.8	0.3	1.0	8	26
Granite Wash	4.8	0.3	1.0	6	21
Eagle Ford	4.9	0.3	1.0	6	20

^a [Mantell \(2011\)](#) reported produced water for the first 10 days at 500,000 to 600,000 gal for the Barnett, Fayetteville and Marcellus Shales.

¹ Flowback estimates may be based on specific time periods (e.g., the flowback during the first 10, 15, or 30 days).

Table 7-2. Additional short-, medium-, and long-term produced water estimates.

Location–formation	Produced water as percentage of injected fluid	Reference	Comment
<i>Estimates without reference to a specific data set</i>			
Unspecified Shale	5% – 35%	Hayes (2011)	
Marcellus Shale	10% – 25%	Minnich (2011)	Initial flowback
ND–Bakken	25%	EERC (2013)	
<i>Estimates with reference to specific data evaluation</i>			
<i>Short duration</i>			
Marcellus Shale	10%	Clark et al. (2013)	0 – 10 days
TX—Barnett	20%	Clark et al. (2013)	0 – 10 days
TX—Haynesville	5%	Clark et al. (2013)	0 – 10 days
AR—Fayetteville	10%	Clark et al. (2013)	0 – 10 days
<i>Mid duration</i>			
WV—Marcellus	8%	Hansen et al. (2013)	30 days
Marcellus Shale	24%	Hayes (2011 , 2009)	Average from 19 wells, 90 days
<i>Long duration</i>			
TX—Barnett	~100% ^a	Nicot et al. (2014)	72 months
WV—Marcellus	10% – 30%	Ziemkiewicz et al. (2014)	Up to 115 months
TX—Eagle Ford	<20%	Nicot and Scanlon (2012)	Lifetime
<i>Unspecified duration</i>			
PA—Marcellus	6%	Hansen et al. (2013)	

^a Approximate median with large variability: 5th percentile of 20% and 90th percentile of 350%.

Table 7-3. Flowback and long-term produced water characteristics for wells in unconventional formations (U.S. EPA, 2015e).Source: ([U.S. EPA, 2015g](#)).

Resource type	Drill type	Fracturing fluid (million gal)			Flowback (percent of fracturing fluid returned)		
		Median	Range	Number of data points	Median	Range	Number of data points
Shale	Horizontal	4.0	0.13–15	50,053	6%	1% – 50%	6,488
	Directional	1.6	0.051–12	124	14%	4% – 31%	19
	Vertical	1.2	0.015–22	4,152	24%	7% – 75%	18
Tight	Horizontal	2.2	0.042–9.4	765	7%	7% – 60%	39
	Directional	0.60	0.056–4.0	693	6%	0% – 60%	263
	Vertical	0.31	0.019–4.0	1,287	8%	1% – 83%	48
Long-term produced water (gal/day per well)							
Shale	Horizontal	900	0–19,000	22,222			
	Directional	480	22–8,700	695			
	Vertical	380	0–4,600	12,393			
Tight	Horizontal	620	0–120,000	2,394			
	Directional	750	12–1,800	3,816			
	Vertical	570	0–4,000	21,393			

- 1 In the following subsections, we first discuss water produced during the flowback period, then
- 2 longer-term produced water.

7.1.1.1. Produced Water during the Flowback Period

- 3 Data were collected from six vertical and eight horizontal wells in the Marcellus Shale of
- 4 Pennsylvania and West Virginia ([Hayes, 2009](#)). The author collected samples of flowback after one,

1 five, and 14 days after hydraulic fracturing was completed, as well as a produced water sample 90
2 days after completion of the wells. Both the vertical and horizontal wells showed their largest
3 volume of flowback between one and five days after fracturing, as shown in Figure 7-1. The wells
4 continued to produce water, and at 90 days, samples were available from four each of the
5 horizontal and vertical wells. The vertical wells produced on average 180 bbl/day (7,600 gal/day or
6 29,000 L/day) and the horizontal wells a similar 200 bbl/day (8,400 gal/day or 32,000 L/day).
7 Results from one Marcellus Shale study were fitted to a power curve, as shown in Figure 7-2
8 ([Ziemkiewicz et al., 2014](#)). These and the [Hayes \(2009\)](#) data show decreasing flowback with time.

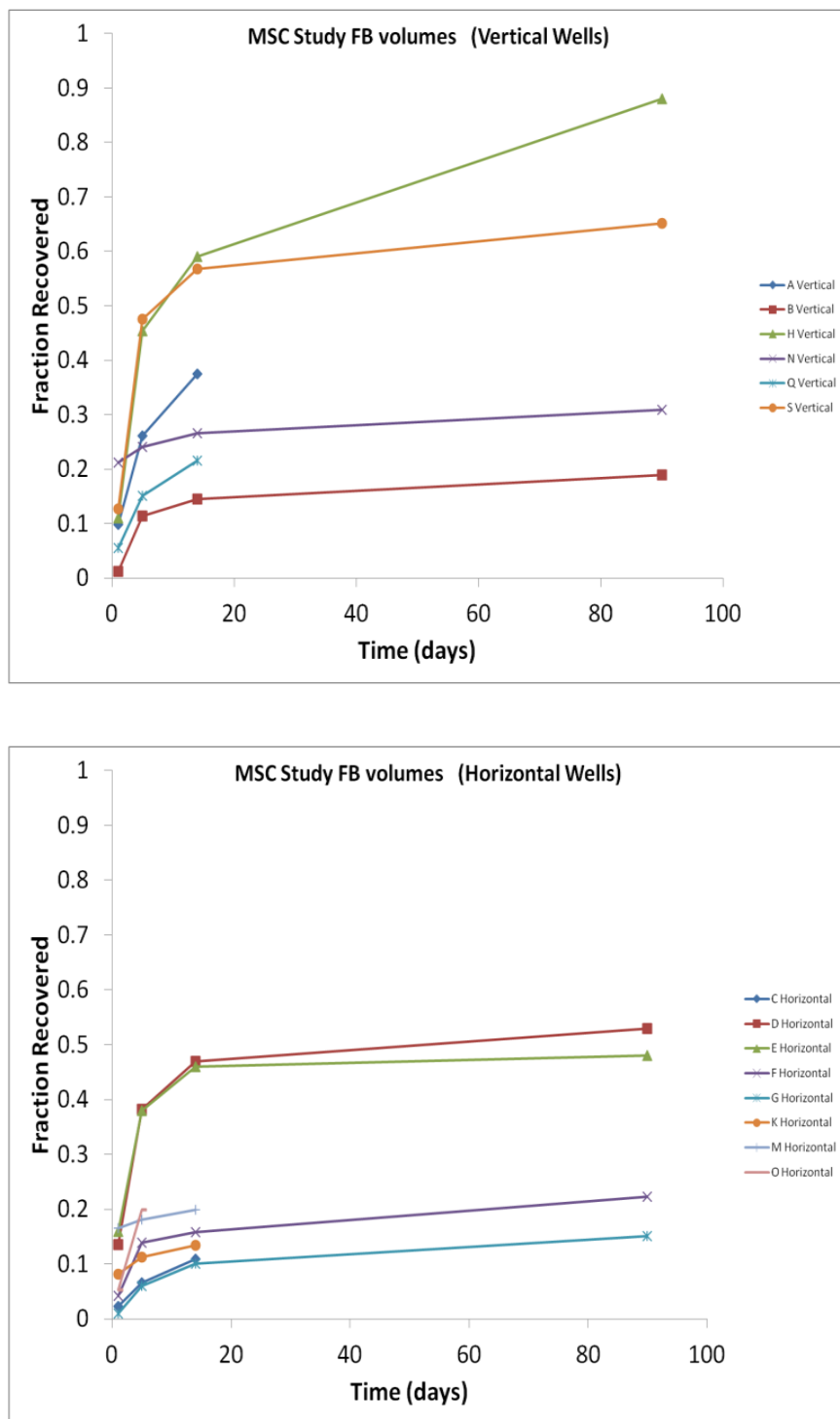


Figure 7-1. Fraction of injected hydraulic fracturing fluid recovered from six vertical (top) and eight horizontal (bottom) wells completed in the Marcellus Shale.

Data from [Hayes \(2009\)](#).

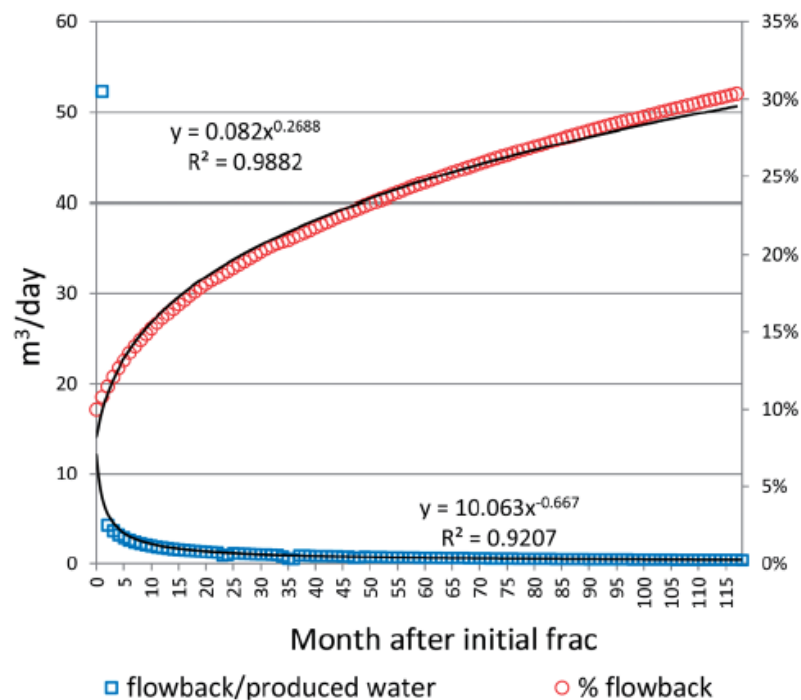


Figure 7-2. Example of flowback and produced water from the Marcellus Shale, illustrating rapid decline in water production and cumulative return of approximately 30% of the volume of injected fluid.

Source: [Ziemkiewicz et al. \(2014\)](#). Reprinted with permission from Ziemkiewicz, P; Quaranta, JD; Mccawley, M. (2014). Practical measures for reducing the risk of environmental contamination in shale energy production. *Environmental Science: Processes & Impacts* 16: 1692-1699. Reproduced by permission of The Royal Society of Chemistry. <http://dx.doi.org/10.1039/C3EM00510K>.

- 1 In West Virginia, water recovered at the surface within 30 days following injection or before 50% of
- 2 the injected fluid volume is returned to the surface is reported as flowback. Data from 271 wells in
- 3 the Marcellus Shale in West Virginia ([Hansen et al., 2013](#)) reveals the variability of recovery from
- 4 wells in the same formation and that the amount of injected fluid recovered was less than 15%
- 5 from over 80% of the wells (see Figure 7-3).

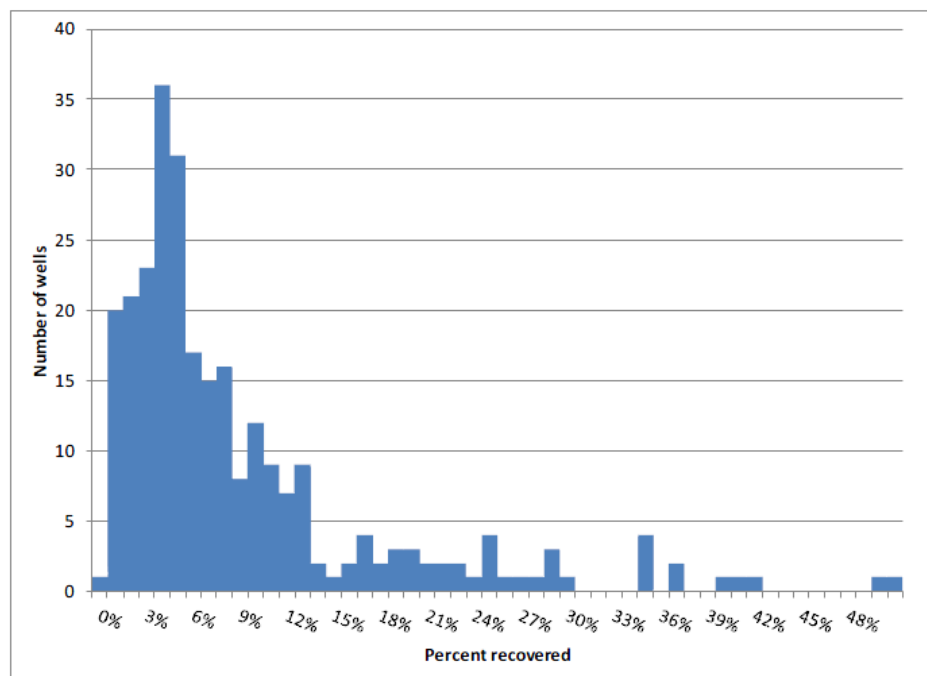


Figure 7-3. Percent of injected fluid recovered for Marcellus Shale wells in West Virginia (2010–2012).

Source: [Hansen et al. \(2013\)](#). One data point showing 98% recovery omitted. Reprinted with permission from Hansen, E; Mulvaney, D; Betcher, M. (2013). Water resource reporting and water footprint from Marcellus Shale development in West Virginia and Pennsylvania. Durango, CO: Earthworks Oil & Gas Accountability Project. Copyright 2013. Permission Downstream Strategies, San Jose State University, and Earthworks Oil & Gas Accountability Project.

The amount of flowback water produced by wells within the first few days of fracturing varies from formation to formation. Wells in the Mississippi Lime and Permian Basin can produce 10 million gal (37.8 million L) in the first 10 days of production. Wells in the Barnett, Eagle Ford, Granite Wash, Cleveland/Tonkawa Sand, Niobrara, Marcellus, and Utica Shales can produce 300,000 to 1 million gal (1.14 to 3.78 million L) within the first 10 days; while Haynesville wells produce less, about 350,000 gal (1.32 million L) ([Mantell, 2013b](#)).

7.1.2. Produced Water

During oil and gas production, other fluids which contain water are produced with hydrocarbons. Throughout this production phase at oil and certain wet gas production facilities, produced water is stored in tanks and pits that may contain free phase, dissolved phase, and emulsified crude oil in the produced water.¹ This crude oil can be present in the produced water container or pit, because the crude oil is not efficiently separated out by the flow-through process vessels (such as three-phase separators, heater treaters, or gun barrels) and passes through to these containers/pits. The

¹ Dry natural gas occurs in the absence of liquid hydrocarbons; wet natural gas typically contains less than 85% methane along with ethane and more complex hydrocarbons ([Schlumberger, 2014](#)).

1 produced water containers and pits containing oil at production facilities are typically regulated
2 under 40 CFR part 112, produced water containers or pits may also be subject to other applicable
3 state and or local laws, regulations and/or ordinances.

4 [Lutz et al. \(2013\)](#) evaluated data reported to the Pennsylvania Department of Environmental
5 Protection (PA DEP) for the time period January 2000 to December 2011. The data were divided
6 between conventional gas wells that might have been hydraulically fractured and hydraulically
7 fractured completions in the Marcellus Shale. The conventional wells produced less drilling water,
8 less flowback (when fractured), and less brine than the shale wells ([Lutz et al., 2013](#); see [Table 1](#)).
9 The average amount of produced water per well was 136,000 gal (514,000 L) for the conventional
10 wells and 1.38 million gal (5.211 million L) for the shale wells. The produced water to gas ratio was
11 1.27 gal (4.8 L) water per MMBtu for the shale wells, which was 2.8 times lower than for
12 conventional wells. Both the produced water and gas produced per well decreased over the four-
13 year period covered by the study. In contrast, conventional oil wells tend to have increased volumes
14 of produced water as they age, and in some cases, older wells may produce five times as much
15 water as new wells ([U.S. GAO, 2012](#)).

16 From experience in several shale formations, [Mantell \(2013b, 2011\)](#) characterized the amount of
17 produced water over the long term as high, moderate, or low. Wells in the Barnett Shale,
18 Cleveland/Tonkawa Sand, Mississippi Lime, and the Permian Basin can produce more than
19 1,000 gal (3,800 L) of water per million cubic feet (MMCF) of gas because of formation
20 characteristics. The most productive of these can be as high as 5,000 gal (19,000 L) per MMCF. As a
21 specific example, a high-producing formation in the western United States was described as
22 producing 4,200 gal (16,000 L) per MMCF for the life of the well ([McElreath, 2011](#)). The well was
23 fractured and stimulated with about 4 million gal (15 million L) of water and returned
24 60,000 gal (230,000 L) per day in the first 10 days, followed by 8,400 gal (32,000 L) per day in the
25 remainder of the first year.

26 Similarly, produced water from horizontal wells in the Barnett Shale decreased rapidly after the
27 wells began producing gas ([Nicot et al., 2014](#)) (see Figure 7-4). The data show a high degree of
28 variability, which was attributed by [Nicot et al. \(2014\)](#) to a few wells with exceptionally high water
29 production. When the produced water data were presented as the percentage of injected fluid, the
30 median exceeded 100% at around 36 months, and the 90th percentile was 350% (see Figure 7-5).
31 This means that roughly 50% of the wells were producing more water than was used in stimulating
32 production. [Nicot et al. \(2014\)](#) noted an inverse relationship between gas and water production but
33 did not identify the source or mechanism for the excess water. Systematic breaching of the
34 underlying karstic Ellenburger Formation was not believed likely; nor was operator efficiency or
35 skill. A number of geologic factors that could impact water migration were identified by ([DOE,](#)
36 [2011a](#)) in the Barnett Shale, including fracture height, aperture size, and density, fracture
37 mineralization, the presence of karst chimneys underlying parts of the Barnett Shale, and others,
38 but the impact of these on water migration was undetermined.

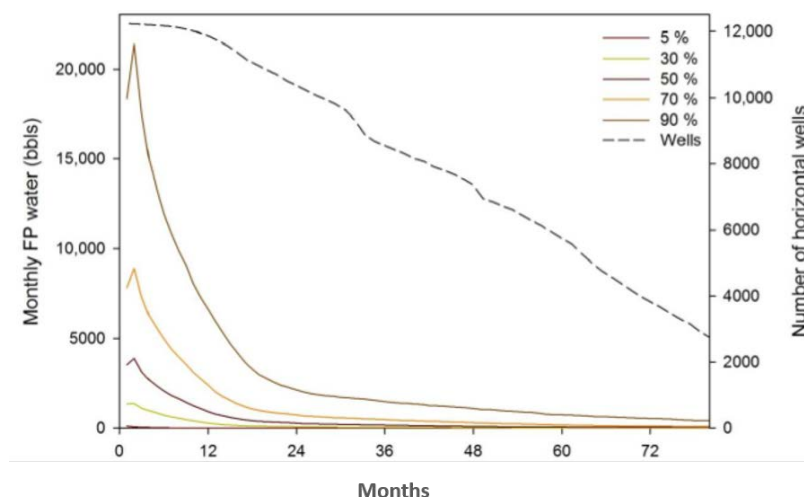


Figure 7-4. Barnett Shale monthly water-production percentiles (5th, 30th, 50th, 70th, and 90th) and number of wells with data (dashed line).

Source: [Nicot et al. \(2014\)](#). FP is the amount of water the flows back to the surface, commingled with water from the formation. Reprinted with permission from [Nicot, JP; Scanlon, BR; Reedy, RC; Costley, RA. \(2014\)](#). Source and fate of hydraulic fracturing water in the Barnett Shale: a historical perspective. *Environ Sci Technol* 48: 2464-2471. Copyright 2014 American Chemical Society.

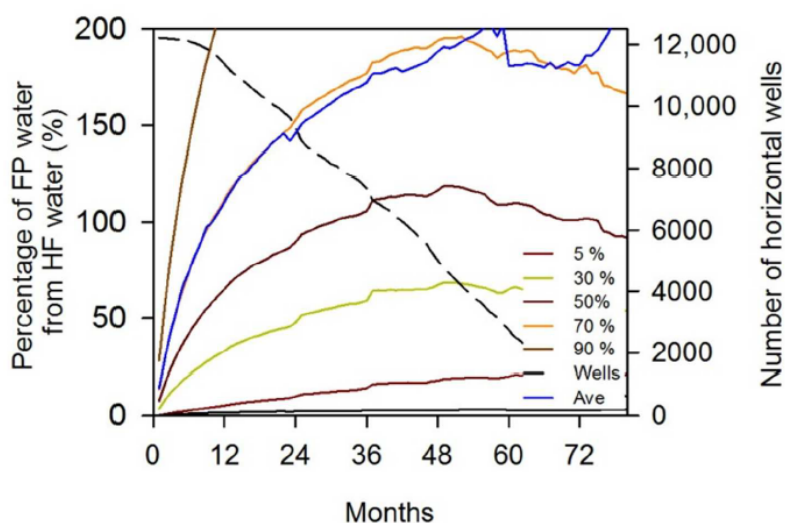


Figure 7-5. Barnett Shale production data for approximately 72 months.

Source: [Nicot et al. \(2014\)](#). Flowback and produced water are reported as the percentage of injected fluid. The dashed line shows the number of horizontal wells included. Data for each percentile show declining production with time, but the median production exceeds 100% of the injected fluid. FP is the amount of water the flows back to the surface, commingled with water from the formation. Reprinted with permission from [Nicot, JP; Scanlon, BR; Reedy, RC; Costley, RA. \(2014\)](#). Source and fate of hydraulic fracturing water in the Barnett Shale: a historical perspective. *Environ Sci Technol* 48: 2464-2471. Copyright 2014 American Chemical Society.

The Niobrara, Granite Wash, Eagle Ford, Haynesville, and Fayetteville Shales are relatively dry and produce between 200 and 2,000 gal (760 to 7,600 L) of produced water per MMCF (Mantell, 2013). The Utica and Marcellus Shales are viewed as drier and produce less than 200 gal (760 L) per MMCF. DOE (2011a) concluded that the characteristic small amount of produced water from the Marcellus Shale was due either to its low water saturation or low relative permeability to water (see Chapter 6). For dry formations, low shale permeability and high capillarity cause water to imbibe into the formation, where it is retained permanently (He, 2011). Engelder (2012) estimated that more than half of the fracturing fluid could be captured within the Marcellus if imbibition drove fluid just 5 cm (2 in) deep into reservoir rocks across the fracture surfaces. This estimate is in agreement with the generalized analysis presented by Byrnes (2011), who estimated depths of 5 to 15 cm (2 to 6 in).

After fracture of coalbeds, water is withdrawn to liberate gas. CBM tends to produce large volumes of water early on: more in fact, than conventional gas-bearing formations (U.S. GAO, 2012). Within producing formations, water production can vary for unknown reasons (U.S. GAO, 2012). Data show that CBM production in the Powder River Basin produces 16 times more water than in the San Juan Basin (U.S. GAO, 2012).

The EPA (2015q) reported characteristics of long-term produced water for shale and tight formations (see Table 7-3). For shale, horizontal wells produced more water (900 gal/day) than vertical wells (380 gal/day). Typically, this would be attributed to the longer length of horizontal laterals than vertical wells, but the data were not normalized to these lengths. The formation-level data used to develop Table 7-3 appear in Table E-1 of Appendix E.

The EPA (2015q) reported that a general rule of thumb is that flowback occurring in the first 30 days of production is roughly equal to the long-term produced water for unconventional formations. As a specific example, from Pennsylvania Marcellus Shale data, the EPA determined that for vertical wells in unconventional formations, 6% of water came from drilling, 35% from flowback, and 59% from long-term produced water; and for horizontal wells the corresponding numbers were 9%, 33%, and 58%. These values deviate from the rule of thumb, because the Marcellus Shale was believed to generate low levels of flowback relative to other formations (U.S. EPA, 2015q).

7.2. Flowback and Produced Water Data Sources

Unlike the evaluation of hydraulic fracturing fluid itself where the chemical composition may be disclosed, knowledge concerning flowback and produced water composition comes from measurements made on samples.

A number of factors are involved in the proper sampling and analyzing of environmental media (U.S. EPA, 2013e; ATSDR, 2005; U.S. EPA, 1992). There may be significant issues obtaining samples, because the specialized equipment used to contain high-pressure natural gas is not designed for producing environmental samples (Coleman, 2011).

To choose the correct analytical methods, it is necessary to have information on:

- Physical state of the sample.
- Identification of analytes of interest.
- Required sensitivity and quantitation limits.
- Analytical objective (i.e., unknown identification, monitoring).
- Required sample containers, preservation, and holding times.

Because some components of hydraulic fracturing fluid are proprietary chemicals, and subsurface reaction products may be unknown, prior knowledge of the identity of analytes may not be available. Consequently, studies may be limited in their ability to determine the presence of either unknown or proprietary constituents contained in flowback or produced water simply because of the lack of knowledge of the identities of the constituents.

After laboratory analysis, the results are evaluated according to quality criteria. Data may be judged to meet applicable quality criteria as determined by the analytical methods or they may be “flagged.” Typically, encountered flags are non-detect, below reporting limit or diluted to meet calibration requirements or because of matrix interference (e.g., [Hayes, 2009](#)).¹ For produced water, a primary interference is from high total dissolved solids (TDS). Interferences also arise from agents which cause foaming and alter surface tension ([Coleman, 2011](#)). Diluted samples result in higher detection limits, and thus lessen ability to identify lower concentrations in samples.

Because of identified limitations in existing methods, the EPA developed new methods for some reported components of hydraulic fracturing fluids, including ethanols and glycols ([U.S. EPA, 2014k](#)), certain nonionic surfactants ([DeArmond and DiGoregorio, 2013a](#)), and acrylamide ([DeArmond and DiGoregorio, 2013b](#)).^{2,3} Each of these methods are applicable to ground and surface waters, and the last ([DeArmond and DiGoregorio, 2013b](#)) to waters with TDS well above 20,000 mg/L.

Generally, analytical methods are impacted by elevated TDS and chloride concentrations, especially inorganic and wet chemistry methods ([Nelson et al., 2014](#); [U.S. EPA, 2014b](#); [Coleman, 2011](#)). Matrix interference impacts standard analysis (EPA Method 8015) for glycols, resulting in high detection limits (10,000 µg/L to 50,000 µg/L) ([Coleman, 2011](#)).

Produced water levels of naturally occurring radionuclides may be 1,000 to 10,000 times the levels of activity found in typical environmental water samples ([U.S. EPA, 2014b](#)). The standard EPA method (Method 900.0) for gross alpha and gross beta involves evaporation of the sample to a layer of residue and analyzing emitted alpha and beta particles. The method has several noted

¹ Matrix interference occurs when components of the sample other than the analyte of interest have an effect on a measurement ([IUPAC, 2014](#)).

² The compounds included were: Diethylene Glycol, Triethylene Glycol, Tetraethylene Glycol, 2-Butoxyethanol and 2-Methoxyethanol.

³ The compounds included were: C12-C16 and C18 alcohol ethoxylates, and alkylphenol ethoxylates.

1 limitations, including known under representation of radium 228, and applicability to drinking
2 water samples with low levels (<500 mg/L) of TDS. As discussed below, produced water can have
3 much higher TDS levels. Because of these limitations, the EPA (2014b) developed an updated
4 method for the detection of gross alpha and gross beta to reduce the matrix interferences, although
5 further improvement is possible.¹

6 Due to the high ionic strength and dissolved solids concentration of flowback water from shale
7 operations, Nelson et al. (2014) similarly found that traditional wet chemistry techniques (EPA
8 Methods 903.0 and 904.0) inefficiently recover radium from samples, with radium-226 recovery
9 sometimes less than 1% . This concern, which could lead to false negatives, was previously noted by
10 Demorest and Wallace (1992). Nelson and coauthors demonstrated that an accurate assessment of
11 flowback radium levels can be performed through nondestructive high-purity germanium gamma
12 spectroscopy and emanation techniques. Studies reporting radium concentrations obtained directly
13 via wet chemistry techniques or studies reporting third-party radium data via wet chemistry
14 techniques may need to be evaluated appropriately as these techniques may underestimate the
15 total radium loads of produced water (Nelson et al., 2014).

16 Data have been generated from specific produced water studies (e.g., Hayes, 2009) or compilations
17 from various sources, such as the USGS produced water database developed in 2002 (Breit, 2002)
18 and updated in 2014 (Blondes et al., 2014). In this database, data were compiled from a variety of
19 sources, some of which we cite as examples below. The data that appear in this chapter and
20 Appendix E are drawn individually from scientific literature and published reports, where
21 necessary we have filled gaps with data from the USGS database.

7.3. Background on Formation Characteristics

22 Subsurface processes and resulting flowback and produced water composition vary depending
23 upon the mineralogy, geochemistry, and structure of formation solids, as well as, residence time
24 and other factors (Dahm et al., 2011; Blauch et al., 2009). The mineralogy and structure of
25 formation solids are determined initially by deposition, when rock grains settle out of their
26 transporting medium (Marshak, 2004). Generally, shale results from clays deposited in deep,
27 oxygen-poor marine environments, and sandstone results from sand deposited in shallow marine
28 environments (Ali et al., 2010; U.S. EPA, 2004). Coal forms when carbon-rich plant matter collects in
29 shallow peat swamps. In the United States, coal is formed in both freshwater and marine
30 environments (NRC, 2010). In the northern Rocky Mountains, coal formed within freshwater
31 alluvial systems of streams, lakes, and peat swamps. In contrast are parts of the Black Warrior
32 formation, which were deposited in brackish and marine settings (Horsey, 1981).

33 Variation in produced water composition follows, in part, from differences in formations which are
34 related to geologic processes. After deposition, physical, chemical, and biological processes occur as

¹ The method developed for determining gross alpha (Th, U, and Po) by liquid scintillation is based on: manganese dioxide coprecipitation followed by group separation of thorium, uranium and polonium on TRU Resin, stripping with ammonium bioxalate, and pulse-shape discrimination liquid scintillation analysis. The average recovery was 74±11% of the known concentration of 230Th with recoveries which ranged from 57% to 104%.

sediments and are consolidated and cemented into rocks in a process called diagenesis. These processes, which can also occur in existing sedimentary rocks, are caused by increased pressure, temperature, and reaction with mineral-rich ground water ([Rushing et al., 2013](#); [Marshak, 2004](#)). Diagenesis may either decrease or increase porosity and permeability through sediment compaction and mineral precipitation, or through grain and cement dissolution ([Ali et al., 2010](#); [Schmidt and McDonald, 1979](#)). Temperature and pressure greatly affect the types and extent of subsurface reactions, influencing the solubility of formation solids, saturation of pore waters, and prevalence of precipitates ([Rushing et al., 2013](#)).

7.4. Flowback Composition

The composition of returning hydraulic fracturing fluid changes with increasing residence time. In this section, we present several examples from individual wells which demonstrate how concentrations approach apparently asymptotic values during the first few days or weeks after hydraulic fracturing.

7.4.1. General Characteristics

Several interacting factors that influence the composition of hydraulic fracturing flowback and produced water are recognized in the scientific literature: (1) the composition of injected hydraulic fracturing fluids, (2) the targeted geological formation and associated hydrocarbon products, (3) the stratigraphic environment, and (4) subsurface processes and residence time ([Barbot et al., 2013](#); [Chapman et al., 2012](#); [Dahm et al., 2011](#); [Blauch et al., 2009](#)).

By design, hydraulic fracturing exposes fresh, organic- and mineral-rich surfaces. Subsurface interactions between injected hydraulic fracturing fluids, formation solids, and formation waters follow. As residence time increases, allowing in situ interactions between injected fluids, formation fluids, and formation solids, changes in the geochemical content of flowback occur such that it still largely reflects that of injected fluids, while later flowback and produced water reflect that of formation-associated fluid ([Rowan et al., 2011](#)).

7.4.2. Temporal Changes in Flowback Composition

Ionic loads, metals, naturally occurring radioactive material (NORM), and organics increase in concentration as water production continues ([Barbot et al., 2013](#); [Murali Mohan et al., 2013](#); [Rowan et al., 2011](#)). The causes include precipitation and dissolution of salts, carbonates, sulfates, and silicates; pyrite oxidation; leaching and biotransformation of organic compounds; and mobilization of NORM and trace elements. Multiple geochemical studies confirm this trend ([Barbot et al., 2013](#); [Haluszczak et al., 2013](#); [Chapman et al., 2012](#); [Davis et al., 2012](#); [Gregory et al., 2011](#); [Blauch et al., 2009](#)).

Concurrent precipitation of sulfates (e.g., BaSO_4) and carbonates (e.g., CaCO_3) alongside decreases in pH, alkalinity, and dissolved carbon load occur over time ([Orem et al., 2014](#); [Barbot et al., 2013](#); [Blauch et al., 2009](#); [Brinck and Frost, 2007](#)). Orem and colleagues showed that organics within CBM produced waters also decrease over time, possibly due to the exhausting of coal-associated waters through formation pumping ([Orem et al., 2007](#)). Decreases in microbial abundance and diversity also occur over time after hydraulic fracturing ([Murali Mohan et al., 2013](#); [Davis et al., 2012](#)).

1 The primary dissolution of native and emplaced salts within the formation and the mobilization of
2 in situ brines constitute the major subsurface processes that control TDS levels in flowback and
3 produced water ([Dresel and Rose, 2010](#); [Blauch et al., 2009](#)).¹ Leaching of organics appears to be a
4 result of injected and formation fluids associating with shale and coal strata ([Orem et al., 2014](#)).

7.4.3. Total Dissolved Solids Enrichment

5 To varying degrees, produced water is enriched in dissolved solids, and the enrichment is
6 dependent upon residence time ([Rowan et al., 2011](#)). As an example, TDS concentrations increased
7 until a limit was reached in flowback and produced water samples from four Marcellus Shale gas
8 wells in three southwestern Pennsylvanian counties ([Chapman et al., 2012](#)) (see Figure 7-6). As is
9 shown in Figure 7-7, TDS in flowback from both Westmoreland County wells became consistent
10 with TDS concentrations cited for typical seawater (35,000 mg/L) within three days, and became
11 consistent with TDS cited for brines (greater than 50,000 mg/L) within five days ([Chapman et al.,
12 2012](#)). TDS concentrations during production exceeded 188,000 mg/L for one well in Greene
13 County. Chapman et al.'s findings are further substantiated by Hayes and colleagues' earlier report
14 of produced water TDS concentrations in 19 Marcellus Shale wells in Pennsylvania and West
15 Virginia ([Hayes, 2009](#)). From an initial injected median value of less than 1,000 mg/L, TDS
16 concentrations increased to a median value exceeding 200,000 mg/L within 90 days ([Hayes, 2009](#)).
17 In the Marcellus Shale, the cation portion of TDS is typically dominated by sodium and calcium,
18 whereas the anion portion is dominated by chloride ([Chapman et al., 2012](#); [Blauch et al., 2009](#)). In
19 section 7.6.4, we note that there is disagreement over whether increased salinity in Marcellus Shale
20 produced water is due to dissolution of salts or mixing of formation water with hydraulic fracturing
21 fluid.

¹ Native salts are formed inside the rock matrix, and can include evaporite minerals such as halite (NaCl), polyhalite (K₂Ca₂Mg(SO₄)₄•2H₂O), celestite (SrSO₄), anhydrite (CaSO₄), kieserite (MgSO₄•H₂O), or sylvite (KCl) ([Blauch et al., 2009](#)). Hydrologic intrusion emplaces salts within formation pores and fractures ([Blauch et al., 2009](#)).

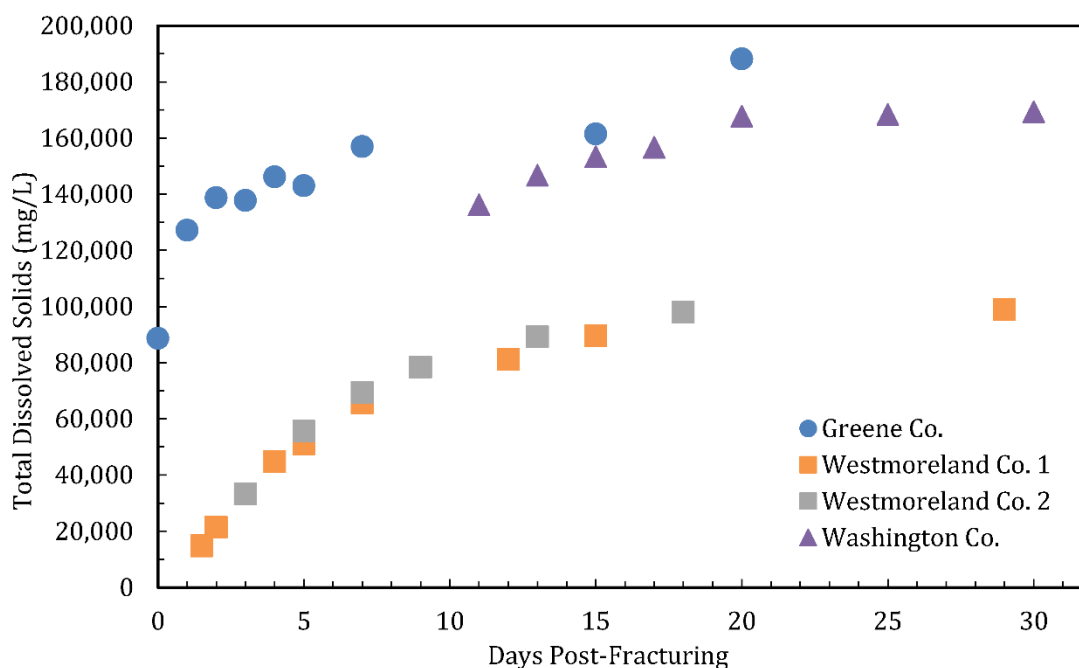


Figure 7-6. TDS concentrations measured through time for injected fluid (at 0 days), flowback, and produced water samples from four Marcellus Shale gas wells in three southwestern Pennsylvania counties.

Data from [Chapman et al. \(2012\)](#).

7.4.4. Radionuclide Enrichment

1 Injected fluids used in hydraulic fracturing typically do not contain radioactive material ([Rowan et](#)
 2 [al., 2011](#)).¹ Shales and sandstones, however, are naturally enriched in various radionuclides, as
 3 described below ([Sturchio et al., 2001](#)). Radium in pore waters or adsorbed onto clay particles and
 4 grain coatings can dissolve and return within flowback ([Langmuir and Riese, 1985](#)). Where data are
 5 available, radium and TDS produced water concentrations are positively correlated with time
 6 passed since hydraulic fracturing ([Rowan et al., 2011](#); [Fisher, 1998](#)). Radium remains adsorbed to
 7 mineral surfaces in low saline environments, and then desorbs with increased salinity into solution
 8 ([Sturchio et al., 2001](#)). Over the course of 20 days, Marcellus Shale produced waters from a gas well
 9 were enriched almost fourfold in radium and from another gas well were enriched over twofold in
 10 TDS concentrations as residence time increased ([Chapman et al., 2012](#); [Rowan et al., 2011](#)) (see
 11 Figure 7-7).

¹ Recycling produced water may introduce radioactive material into hydraulic fracturing fluid. See section 8.4.3 and [PA DEP \(2015b\)](#).

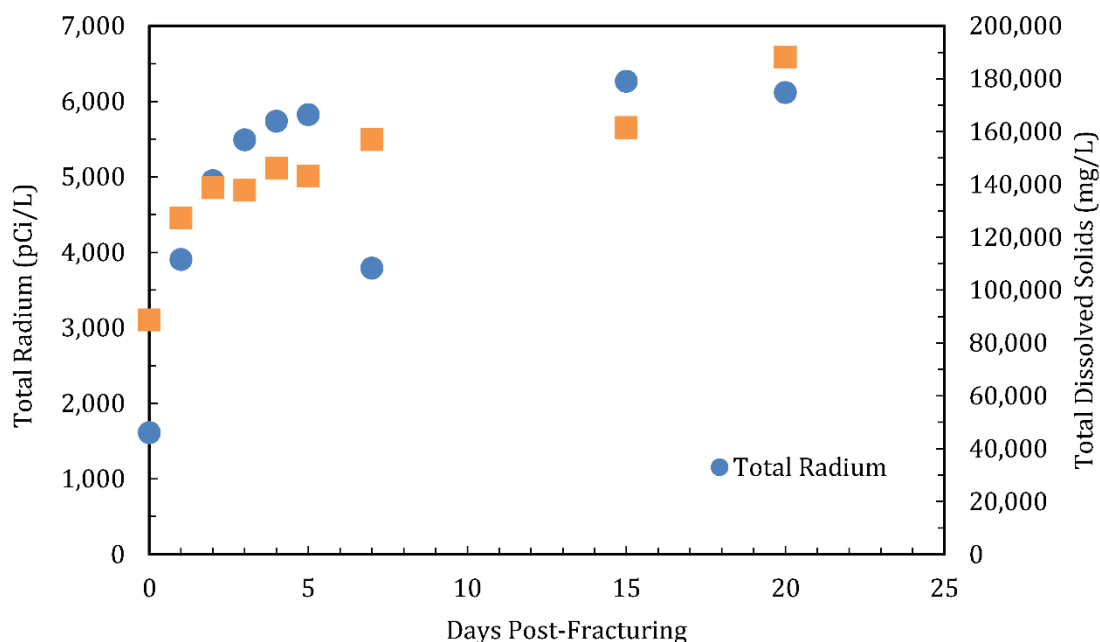


Figure 7-7. Total radium and TDS concentrations measured through time for injected (day 0), flowback, and produced water samples from mutually exclusive Greene County, PA, Marcellus Shale gas wells.

Data from [Rowan et al. \(2011\)](#) and [Chapman et al. \(2012\)](#).

7.4.5. Leaching and Biotransformation of Naturally Occurring Organic Compounds

Many organics are known to leach naturally into formation water through association with shale, sandstone, and coal strata ([Benko and Drewes, 2008](#); [Orem et al., 2007](#)). [Orem et al. \(2014\)](#) show that formation and produced waters from shale plays that were not impacted by production chemicals contain an array of organic compound classes associated with the formation. When unconventional formations are hydraulically fractured, additional organics from the freshly fractured hydrocarbon-bearing formation and the chemical additives contribute to a large increase in flowback and produced water organic loads ([Orem et al., 2014](#)).

The nature of the in-situ hydrocarbons reflects the formation's thermal maturity and heavily influences the organic content of the produced water.¹ The Marcellus Shale is largely considered a mature formation and therefore consists of wet and dry gas ([Barbot et al., 2013](#); [Repetski et al., 2008](#)). Conversely, the Utica Shale is less thermally mature; available hydrocarbon resources consist of oil, condensate, and gas ([Repetski et al., 2008](#)). Additionally, some coals within the eastern and west-central regions of the San Juan Basin produce little to no water during production, due to the regional thermal maturity, hydrostratigraphy, and in situ trapping mechanisms ([New Mexico Bureau of Mines and Mineral Resources, 1994](#)).

¹ With increasing subsurface temperature after burial, petroleum source material (kerogen) produces hydrocarbons in a sequence from methane (immature), to oil (more mature), to gas (mature). Gas is produced by thermal cracking of oil ([PA DCNR, 2015](#)).

Dissolved organic carbon (DOC) concentrations decrease from hydraulic fracturing through flowback in shales and coalbeds ([Murali Mohan et al., 2013](#); [Orem et al., 2007](#)). DOC sorption, dilution with injected or formation water, biochemical reactions, and microbial transformation (i.e., biotransformation in the form of degradation or uptake) may all cause decreased concentrations of DOC during flowback. Organic chemical additives injected during hydraulic fracturing offer a novel carbon and energy source for biotic and abiotic reactions at depth. Injected organics include many sugar-based polymer formulations, most notably of galactose and mannose (i.e., guar gum used as a gelling agent); hydrocarbon distillates used in crosslinkers, friction reducers, and gelling agents; and ethyl and ether glycol formulations used in non-emulsifiers, crosslinkers, friction reducers, and gelling agents. ([Wuchter et al., 2013](#); [Arthur et al., 2009b](#); [Hayes, 2009](#)).

DOC and chloride concentrations exhibit strongly correlated inverse temporal trends ([Barbot et al., 2013](#); [Chapman et al., 2012](#)) for flowback and produced water samples obtained from three Marcellus Shale wells from the same well pad in Greene County, Pennsylvania ([Cluff et al., 2014](#)), as shown in Figure 7-8. Chloride concentrations increased five- to six-fold as a function of residence time (i.e., cumulative volumes of produced water). These chloride concentrations followed an increasing linear trend during the first two weeks of flowback (see Figure 7-8a, inset) then began to approach asymptotic levels later in production, indicating that injected fluids had acquired a brine signature as a result of subsurface mixing, fluid-solid interactions, and mineral dissolution processes.

DOC concentrations exhibit an inverse trend and decreased through flowback and production (Figure 7-8b) ([Cluff et al., 2014](#)). DOC levels decreased approximately twofold between injected fluid and initial flowback samples (Figure 7-8b, inset). DOC concentrations decreased by 11-fold over the study's time frame (nearly 11 months) and leveled off several months after hydraulic fracturing, presumably as a result of in situ attenuation processes ([Cluff et al., 2014](#)).

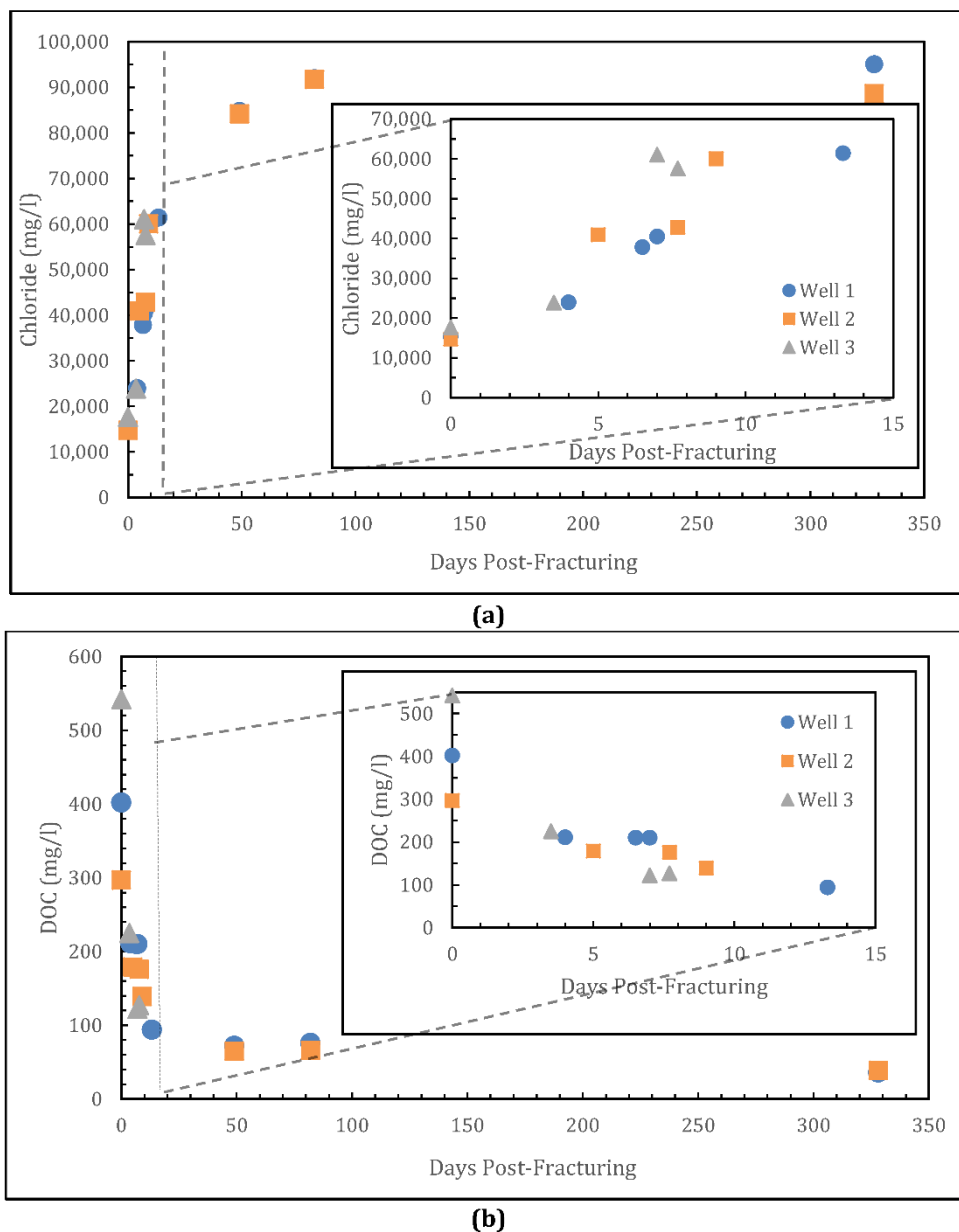


Figure 7-8. (a) Chloride (Cl) and (b) DOC concentrations measured through time for injected (day 0), flowback, and produced water samples obtained from three Marcellus Shale gas wells from a single well pad in Greene County, PA used for hydraulic fracturing.

Data from [Cluff et al. \(2014\)](#). Reprinted with permission from Cluff, M; Hartsock, A; Macrae, J; Carter, K; Mouser, PJ. (2014). Temporal changes in microbial ecology and geochemistry in produced water from hydraulically fractured Marcellus Shale Gas Wells. Environ Sci Technol 48: 6508-6517. Copyright 2014 American Chemical Society.

[Orem et al. \(2014\)](#) conducted a temporal study of two coalbed wells over the course of one year. Their results suggest that organic compound concentrations decrease over time. This trend may be due to pumping of water to the surface, which may exhaust coal-associated produced water. Subsequent produced water would not be associated with the coal. This suggests that the early produced water would contain the highest organic load ([Orem et al., 2014](#)).

As noted above, most literature addresses general organic parameters such as bulk total organic carbon (TOC) or DOC instead of individual organic compounds ([Sirivedhin and Dallbauman, 2004](#)). Emphasis on the prevalence of bulk organics as opposed to unique organics is due largely to the lack of analytical standards for many compounds and also a lack of knowledge regarding the types of organics to test in produced water samples ([Schlegel et al., 2013](#); [Strong et al., 2013](#)).

7.5. Produced Water Composition

In this section, we discuss the characteristics of aggregated produced water data without regard for temporal changes. Similarities between conventional and unconventional produced water are noted and the variability between formation types is described. As we discuss below, produced water may contain a range of constituents, but in widely varying amounts. Generally, these may include:

- Salts, including those composed from chloride, bromide, sulfate, sodium, magnesium and calcium.
- Metals including barium, manganese, iron, and strontium.
- Dissolved organics including BTEX and oil and grease.
- Radioactive materials including radium (radium-226 and radium-228).
- Hydraulic fracturing chemicals and their transformation products.

We discuss these groups of chemicals and then conclude by discussing variability within formation types and within production zones.

7.5.1. Similarity of Produced Water from Conventional and Unconventional Formations

Unconventional produced water is reported to be similar to conventional produced waters in terms of TDS, pH, alkalinity, oil and grease, TOC, and other organics and inorganics ([Wilson, 2014](#); [Haluszczak et al., 2013](#); [Alley et al., 2011](#); [Hayes, 2009](#); [Sirivedhin and Dallbauman, 2004](#)). Although salinity varies in shales and tight formations, produced water is typically characterized as saline ([Lee and Neff, 2011](#); [Blauch et al., 2009](#)). Produced water is also enriched in major anions (e.g., chloride, bicarbonate, sulfate), cations (e.g., sodium, calcium, magnesium), metals (e.g., barium, strontium), naturally occurring radionuclides (e.g., radium-226 and radium-228) ([Chapman et al., 2012](#); [Rowan et al., 2011](#)), and organics (e.g., hydrocarbons) ([Orem et al., 2007](#); [Sirivedhin and Dallbauman, 2004](#)).

7.5.2. Variability in Produced Water Composition Among Unconventional Formation Types

[Alley et al. \(2011\)](#) compared geochemical parameters of shale gas, tight gas, and CBM produced water. This comparison aggregated data on produced water from original analyses, peer-reviewed

literature, and public and confidential government and industry sources and determined the statistical significance of the results. As shown in Table 7-4, [Alley et al. \(2011\)](#) found that of the constituents of interest common to all three types of unconventional produced water (calcium, chloride, potassium, magnesium, manganese, sodium, and zinc):

- 1) Shale gas produced water had significantly different concentrations from those of CBM;
- 2) Shale gas produced water constituent concentrations were significantly similar to those of tight gas, except for potassium and magnesium; and
- 3) Five tight gas produced water constituent concentrations (calcium, chloride, potassium, magnesium, and sodium) were significantly similar to those of CBM ([Alley et al., 2011](#)).

The degree of variability between produced waters of these three resource types is consistent with the degree of mineralogical and geochemical similarity between shale and sandstone formations, and the lack of the same between shale and coalbed formations ([Marshak, 2004](#)).

Table 7-4. Compiled minimum and maximum concentrations for various geochemical constituents in unconventional shale gas, tight gas, and CBM produced water (Alley et al., 2011).

Source: ([Alley et al., 2011](#)).

Parameter	Unit	Shale gas ^a	Tight gas ^b	CBM ^c
Alkalinity	mg/L	160–188	1,424	54.9–9,450
Ammonium-N	mg/L	-	2.74	1.05–59
Bicarbonate	mg/L	ND–4,000	10–4,040	-
Conductivity	µS/cm	-	24,400	94.8–145,000
Nitrate	mg/L	ND–2,670	-	0.002–18.7
Oil and grease	mg/L	-	42	-
pH	SU ^d	1.21–8.36	5–8.6	6.56–9.87
Phosphate	mg/L	ND–5.3	-	0.05–1.5
Sulfate	mg/L	ND–3,663	12–48	0.01–5,590
Radium-226	pCi/g	0.65–1.031	-	-
Aluminum	mg/L	ND–5,290	-	0.5–5,290
Arsenic	mg/L	-	0.17	0.0001–0.06
Boron	mg/L	0.12–24	-	0.002–2.4
Barium	mg/L	ND–4,370	-	0.01–190

Parameter	Unit	Shale gas ^a	Tight gas ^b	CBM ^c
Bromine	mg/L	ND–10,600	-	0.002–300
Calcium	mg/L	0.65–83,950	3–74,185	0.8–5,870
Cadmium	mg/L	-	0.37	0.0001–0.01
Chlorine	mg/L	48.9–212,700	52–216,000	0.7–70,100
Chromium	mg/L	-	0.265	0.001–0.053
Copper	mg/L	ND–15	0.539	ND–0.06
Fluorine	mg/L	ND–33	-	0.05–15.22
Iron	mg/L	ND–2,838	0.015	0.002–220
Lithium	mg/L	ND–611	-	0.0002–6.88
Magnesium	mg/L	1.08–25,340	2–8,750	0.2–1,830
Manganese	mg/L	ND–96.5	0.525	0.002–5.4
Mercury	mg/L	-	-	0.0001–0.0004
Nickel	mg/L	-	0.123	0.0003–0.20
Potassium	mg/L	0.21–5,490	5–2,500	0.3–186
Sodium	mg/L	10.04–204,302	648–80,000	8.8–34,100
Strontium	mg/L	0.03–1,310	-	0.032–565
Uranium	mg/L	-	-	0.002–0.012
Zinc	mg/L	ND–20	0.076	0.00002–0.59

-, no value available; ND, non-detect. If no range, but a singular concentration is given, this is the maximum concentration.

^a *n* = 541. [Alley et al. \(2011\)](#) compiled data from [USGS \(2006\)](#); [McIntosh and Walter \(2005\)](#); [McIntosh et al. \(2002\)](#) and confidential industry documents.

^b *n* = 137. [Alley et al. \(2011\)](#) compiled data from [USGS \(2006\)](#) and produced water samples presented in [Alley et al. \(2011\)](#).

^c [Alley et al. \(2011\)](#) compiled data from [Montana GWIC \(2009\)](#); [Thordsen et al. \(2007\)](#); [ESN Rocky Mountain \(2003\)](#); [Rice et al. \(2000\)](#); [Rice \(1999\)](#); [Hunter and Moser \(1990\)](#).

^d SU = standard units.

- 1 Shale gas produced water tends to be more acidic, as well as, enriched in strontium, barium, and
- 2 bromide. CBM produced water is highly alkaline, and it contains relatively low concentrations of
- 3 TDS (one to two orders of magnitude lower than in shale and sandstone). It also contains lower
- 4 levels of sulfate, calcium, magnesium, DOC, sodium, bicarbonate, and oil and grease than typically

observed in shale and sandstone produced waters ([Alley et al., 2011](#); [Dahm et al., 2011](#); [Benko and Drewes, 2008](#); [Van Voast, 2003](#)).¹

7.5.3. General Water Quality Parameters

For this assessment, the EPA identified data characterizing the content of unconventional flowback and produced water in a total of 12 shale and tight formations and CBM basins. These formations and basins span 18 states. Note that in this subsection we treat all fluids as produced. As a consequence, the variability of reported concentrations is likely higher than if the data could be standardized to a specific point on the flowback-to-produced water continuum.

For most formations, the amount of general water quality parameter data is variable (see Table E-2 of Appendix E). Average pH levels range from 5.87 to 8.19, with typically lower values for shales. Larger variations in average specific conductivity are seen among unconventional formations and range from 213 microsiemens (μS)/cm in the Bakken Shale to 184,800 μS /cm in Devonian sandstones (see Table E-2 of Appendix E). Shale and tight formation produced waters are enriched in suspended solids, as reported concentrations for total suspended solids and turbidity exceed those of coalbeds by one to two orders of magnitude.

Of the data presented in Table E-3 of Appendix E, differences are evident between the Black Warrior and the three western formations (Powder River, Raton, and San Juan). The Black Warrior is higher in average chloride, specific conductivity, TDS, TOC and total suspended solids; and lower in alkalinity and bicarbonate than the other three. These differences are due to the saline or brackish conditions during deposition in the Black Warrior that contrast to the freshwater conditions for the western basins.

The average dissolved oxygen (DO) concentrations of CBM produced water range from 0.39-1.07 mg/L (see Table E-3 Appendix E). By comparison, well-oxygenated surface water can contain up to 10 mg/L DO at 15 °C ([U.S. EPA, 2012a](#)). Thus, coalbed produced water is either hypoxic (less than 2 mg/L DO) or anoxic (less than 0.5 mg/L DO) and could contribute to aquatic organism stress ([USGS, 2010](#); [NSTC, 2000](#)).

7.5.4. Salinity and Inorganics

The TDS profile of unconventional produced water is dominated by sodium and chloride, with large contributions to the profile from mono- and divalent cations ([Sun et al., 2013](#); [Guerra et al., 2011](#)). In order of relative abundance, the following inorganic ions are typically found in highly saline conventional produced water: sodium, chloride, calcium, magnesium, potassium, sulfate, bromide, strontium, bicarbonate, and iodide ([Lee and Neff, 2011](#)). Shale and sandstone produced water tend to be characterized as sodium-chloride-calcium water types, whereas CBM produced water tends to be characterized as sodium chloride or sodium bicarbonate water types ([Dahm et al., 2011](#)). Elevated levels of bromide, sulfate, and bicarbonate are also present ([Sun et al., 2013](#)). Elevated strontium and barium levels are characteristic of Marcellus Shale flowback and produced water

¹ Several had low representation in the [Alley et al. \(2011\)](#) data set, including the Appalachian Basin (western New York and western Pennsylvania), West Virginia, eastern Kentucky, eastern Tennessee, and northeastern Alabama.

([Barbot et al., 2013](#); [Haluszczak et al., 2013](#); [Chapman et al., 2012](#)). Data representing shales and tight formations are presented in Table E-4 of Appendix E.

[Rowan et al. \(2015\)](#) acknowledge that the origin of saline water produced from the Marcellus Shale is a matter of debate. One idea is that injected fluid returns at higher salinity, because of dissolving halite and other minerals found in shale ([Blauch et al., 2009](#)). Blauch and colleagues hypothesized that salt layers bearing barium, calcium, iron, potassium, magnesium, sodium, and strontium likely dissolve and contribute to flowback and produced water salinity ([Blauch et al., 2009](#)). However, actual mixing of formation water and fracturing fluid was postulated by [Haluszczak et al. \(2013\)](#) from arguments based on the near-neutral pH and low levels of chloride and sulfate in the Marcellus data from [Hayes \(2009\)](#), as well as, the relationship between chloride and bromide. Engle and Rowan determined that water chemistry during the first 90 days of production is controlled by mixing of injected and formation waters and stimulation of bacterial sulfate reduction ([Engle and Rowan, 2014](#); [Haluszczak et al., 2013](#)). [Rowan et al. \(2015\)](#) argue, based on an observed shift to isotopically heavier water, that produced water actually contains formation water.¹ Alternately, [Barbot et al. \(2013\)](#) concluded from analysis of Marcellus Shale produced water that mixing (with formation water) alone could not explain the observed patterns in chloride concentrations.

Marcellus Shale produced water salinities range from less than 1,500 mg/L to over 300,000 mg/L, as shown by [Rowan et al. \(2011\)](#). By comparison, the average salinity concentration for seawater is 35,000 mg/L. The TDS concentration of CBM produced water can be as low as 500 mg/L ranging to nearly 50,000 mg/L ([Dahm et al., 2011](#); [Benko and Drewes, 2008](#); [Van Voast, 2003](#)). Lower dissolved solids are expected from CBM produced water, in part, because some coals developed in fresh water environments ([Bouska, 1981](#)). [Dahm et al. \(2011\)](#) report TDS concentrations from a composite CBM produced water database ($n = 3,255$) for western basins that often are less than 5,000 mg/L (85% of samples). In other cases, as for the Black Warrior basin, TDS can be higher along with concentrations of species that contribute to TDS (See Table E-5 Appendix E), such as calcium, chloride, and sodium.

7.5.5. Metals

The metals content of unconventional produced water varies by well and site lithology, but is typically dominated by the same metals that are associated with conventional produced water. Unconventional produced water may also contain low levels of heavy metals (e.g., chromium, copper, nickel, zinc, cadmium, lead, arsenic, and mercury) ([Hayes, 2009](#)). Data illustrating metal concentrations in produced water appear in Tables E-6 and E-7 of Appendix E.

¹ The produced water becomes isotopically heavier because of increased prevalence of Oxygen-18 in the water, compared to the more prevalent Oxygen-16.

7.5.6. Naturally Occurring Radioactive Material (NORM) and Technologically Enhanced Naturally Occurring Radioactive Material (TENORM)

7.5.6.1. Formation Solids Levels of NORM

Elevated uranium levels in formation solids have been used to identify potential areas of natural gas production for decades ([Fertl and Chilingar, 1988](#)). Marine black shales are estimated to contain an average of 15–60 ppm uranium depending on depositional conditions ([Fertl and Chilingar, 1988](#)). Shales that bear significant levels of uranium include the Barnett in Texas, the Woodford in Oklahoma, the New Albany in the Illinois Basin, the Chattanooga Shale in the southeastern United States, and a group of black shales in Kansas and Oklahoma ([Swanson, 1955](#)).

7.5.6.2. Produced Water Levels of TENORM

When exposed to the environment or concentrated NORM is termed technologically-enhanced naturally-occurring radioactive material (TENORM).¹ Radioactive materials commonly present in shale and sandstone sedimentary environments include uranium, thorium, radium, and their decay products. These are present in most unconventional produced water, but particularly so in Marcellus Shale produced water ([Rowan et al., 2011](#); [Fisher, 1998](#)). Low levels of uranium and thorium return during flowback, typically in the concentrated form of mineral phases or organic matter, due to insolubility under prevailing reducing conditions encountered within shale formations ([Nelson et al., 2014](#); [Sturchio et al., 2001](#)).

Conversely, radium, a decay product of uranium and thorium, is known to be relatively soluble within the redox range encountered in subsurface environments ([Sturchio et al., 2001](#); [Langmuir and Riese, 1985](#)). Dissolved radium primarily occurs as Ra^{2+} , but it complexes with carbonate, chloride, and sulfate ions as well ([Sturchio et al., 2001](#); [Langmuir and Riese, 1985](#)). Ra^{2+} can also substitute for various cations (e.g., Ba^{2+} , Ca^{2+} , and Sr^{2+}) during mineral precipitation, as is sometimes the case with barite or anhydrite precipitation ([Rowan et al., 2011](#)).

Data from the Marcellus Shale show that radium and TDS produced water concentrations are positively correlated ([Rowan et al., 2011](#); [Fisher, 1998](#)). This pattern is expected for other formations because radium remains adsorbed to mineral surfaces in low salinity environments, then desorbs as solution salinity increases ([Sturchio et al., 2001](#)). Controlling for this TDS dependence, Marcellus Shale produced water contains statistically more radium than non-Marcellus Shale produced water, with a median total radium content of 2,460 picocuries per liter (pCi/L) ($n = 52$) compared to 1,011 pCi/L ($n = 91$), respectively ([Rowan et al., 2011](#)). Radium levels in Marcellus produced water are at several thousand picocuries per liter, with maximum concentrations of total radium (radium-226 and radium-228), radium-226 and radium-228 reported at approximately 18,000, 9,000, and 1,300 pCi/L, respectively ([Rowan et al., 2011](#)) (see Table E-8 in Appendix E). Data from the Pennsylvania TENORM produced water study (PA DEP,

¹ The U.S. EPA Office of Radiation (<http://www.epa.gov/radiation/tenorm/>) states that technologically enhanced naturally occurring radioactive material (TENORM) is produced when activities such as uranium mining, or sewage sludge treatment, concentrate or expose radioactive materials that occur naturally in ores, soils, water, or other natural materials. Formation water containing radioactive materials would contain NORM, because they are not exposed; produced water would contain TENORM because it has been exposed to the environment.

2015) showed similar elevated levels, and consistently showed higher medians in unconventional compared to conventional formations (Table E-8 in Appendix E).

7.5.7. Organics

The organic content of produced water varies by well and lithology, but consists of certain naturally occurring and injected organic compounds. These organics may be dissolved in water or, for the case of oil production, in the form of a separate or emulsified phase. Produced water organics can contain any of the following: (1) volatile organic compounds (VOCs) such as benzene and toluene, (2) semi-volatile organic compounds (SVOCs) such as phenols; and/or (3) non-VOCs such as macromolecular natural organic matter ([Orem et al., 2014](#); [Hayes, 2009](#); [Benko and Drewes, 2008](#); [Orem et al., 2007](#); [Sirivedhin and Dallbauman, 2004](#)). Table 7-5 presents data from naturally occurring organic chemicals in produced water.

Table 7-5. Concentration ranges (mg/L) of several classes of naturally occurring organic chemicals in conventional produced water worldwide (reported in Neff, 2002).

Source: ([Neff, 2002](#))

Chemical class	Concentration range (mg/L)
TOC	≤0.1–>11,000
Total organic acids	≤0.001–10,000
Total saturated hydrocarbons	17–30
Total benzene, toluene, ethylbenzene, and xylenes (BTEX)	0.068–578
Total PAH	0.040–3
Total steranes/triterpanes	0.140–0.175
Ketones	1–2
Total phenols (primarily C ₀ –C ₅ phenols)	0.400–23

Several classes of naturally occurring organic chemicals are present in conventional and unconventional produced waters, with large concentration ranges ([Lee and Neff, 2011](#)). In addition to data on total organic carbon (TOC) and dissolved organic carbon (DOC) as indicators of the presence of organics, specifically identified organics include saturated hydrocarbons, BTEX, and polycyclic aromatic hydrocarbon (PAHs) (see Table E-9 of Appendix E). Data are lacking on the presence and concentration of many other types of organic chemicals that might be present in produced water, because of their use in hydraulic fracturing fluid. There are a number of reasons for this difference, some of which could be related to analytical limitations, limited focus of produced water studies, and undocumented subsurface reactions.

7.5.8. Reactions within Formations

The introduction of hydraulic fracturing fluids into the target formation induces a number of changes to formation solids and fluids that influence the chemical evolution and composition of

flowback and produced water. These changes can result from physical processes (e.g., rock fracturing and fluid mixing) and geochemical processes (e.g., introducing novel, oxygenated fluids) that mobilize trace or major constituents into solution.

The creation of fractures exposes new formation surfaces to interactions involving hydraulic fracturing fluids and existing formation fluids. Formations targeted for unconventional development are composed of detrital, cement, and organic fractions. For example, elements potentially available for mobilization when exposed via fracturing include calcium, magnesium, manganese, and strontium in cement fractions, and silver, chromium, copper, molybdenum, niobium, vanadium, and zinc in organic fractions. The storage or release of these elements in newly exposed surfaces is variable and not well studied, in part due to the vast number of possible interactions occurring continuously in the environment at the rock surface ([Vine and Tourtelot, 1970](#)).

Contact with and physical mixing of hydraulic fracturing fluids with existing formation brines also influences the geochemical evolution of produced water. For instance, Marcellus Shale brines have high concentrations of bromide, calcium, chloride, magnesium, sodium, and strontium ([Engle and Rowan, 2014](#)). Hydraulic fracturing fluid contains elevated levels of DOC, alkalinity, and sulfate ([Engle and Rowan, 2014](#)). Consequently, flowback acquires a geochemical signature reflecting both injected and formation fluids. Produced water containing both Although some constituents of hydraulic fracturing fluids are known to readily degrade in the environment, little is known regarding how the subsurface degradation proceeds or how the constituents interact within a complex matrix of organics ([Mouser et al., In Press](#)).

7.6. Spatial Trends

As was reported for the volume of produced water (see Section 7.2.2), the composition of produced water varies spatially on a regional to local scale according to the geographic and stratigraphic locations of each well within a hydraulically fractured formation ([Bibby et al., 2013](#); [Lee and Neff, 2011](#)). Spatial variability of produced water content occurs (1) between plays of different rock sources (e.g., coal vs. sandstone), (2) between plays of the same rock type (e.g., Barnett Shale vs. Bakken Shale), and (3) within formations of the same source rock (e.g., northeastern vs. southwestern Marcellus Shale) ([Barbot et al., 2013](#); [Alley et al., 2011](#); [Breit, 2002](#)).

Geographic variability in produced water content has been established at a regional scale for conventional produced water. As an example, [Benko and Drewes \(2008\)](#) demonstrate TDS variability in conventional produced water among fourteen western geologic basins (e.g., Williston, San Juan, and Permian Basins). Median TDS in these basins range from as low as 4,900 mg/L in the Big Horn Basin to as high as 132,400 mg/L in the Williston Basin based on over 133,000 produced water samples from fourteen basins ([Benko and Drewes, 2008](#)).¹

¹ Data were drawn from the USGS National Produced Water Geochemical Database v2.0. Published updates made in October 2014 to the database (v2.1) are not reflected in this document.

High TDS (more than 200,000 ppm) is common throughout the central portion of the United States in various basins. Low TDS (<10,000 ppm) was found in the basins of the Rocky Mountains, and sometimes in Texas and California. In other areas, there was a mixture of mid-range, which in the case of Illinois was correlated to the depth of producing zones ([Breit, 2002](#)).

Data further illustrating variability within shale, tight-gas and coalbed formations at both the formation and local scales are presented and discussed in Section E-3 of Appendix E.

7.7. Spill Impacts on Drinking Water Resources

Surface spills of flowback and produced water from unconventional oil and gas production have occurred across the country and in some cases have caused impacts to drinking water resources, as described in this section. Released fluids, if not contained on-site, may flow into nearby surface waters or infiltrate into ground water via soil. In this section, we first briefly describe the potential for spills from produced water handling equipment. Next, we address individually-reported spill events. These have originated from pipeline leaks, well blowouts, well communication events, and leaking pits and impoundments. We then summarize several studies of aggregated spill data, most of which are based on state agency spill reports. The section concludes with discussion of two cases.

7.7.1. Produced Water Management and Spill Potential

Produced water is typically transported from the wellhead through a series of pipes or flowlines to on-site storage or treatment units ([GWPC and IOGCC, 2014](#)). Faulty connections at either end of the transfer process or leaks or ruptures in the lines carrying the fluid can result in surface spills.

Recovered fluids may be transferred to surface impoundments for long-term storage and evaporation. Surface impoundments are typically uncovered earthen pits that may or may not be lined. Recovered fluids may overflow from surface impoundments due to improper pit design and weather events.

Produced water that is to be treated or disposed of off-site is typically stored in storage tanks or impoundments until it can be loaded into transport trucks for removal ([Gilmore et al., 2013](#)). Tank storage systems are typically closed loop systems in which produced water is transported from the wellhead to aboveground storage tanks through interconnecting pipelines ([GWPC and IOGCC, 2014](#)). Failure of connections and lines during the transfer process or the failure of a storage tank can result in a surface release of fluids.

Depending on its characteristics, produced water, may be recycled and reused on-site. It can be directly reused without treatment (after blending with freshwater) or it can be treated on-site prior to reuse ([Boschee, 2014](#)). As with other flowback management options, these systems also present spill potential during transfer of fluids.

7.7.2. Spills of Hydraulic Fracturing Flowback and Produced Water from Unconventional Oil and Gas Production

7.7.2.1. Pipeline Leaks

In some locations, pipelines are used to transport produced water. Aggregated information on pipeline leaks from the whole country is not available. This section, rather, contains examples of incidents that have occurred. A leak was detailed in a field report from [PA DEP \(2009a\)](#), which described a leak from a 90-degree bend in an overland pipe carrying a mixture of flowback and freshwater between two impoundments. Along a 0.4 mi (0.6 km) length of the impacted stream, 168 fish and 6 salamanders were killed; beyond a confluence at 0.6 km with a creek no additional dead fish were found. The release was estimated at 250 bbl (11,000 gal or 40,000 L). In response to the incident, the pipeline was shut off, a dam was constructed for recovering the water, water was vacuumed from the stream, and the stream was flushed with fresh water ([PA DEP, 2009a](#)).

In January 2015, 70,000 barrels (2,940,000 gal or 11,130,000 L) of produced water containing petroleum hydrocarbons ([North Dakota Department of Health, 2015](#)) were released from a broken pipeline that crosses Blacktail Creek in Williams County, ND. The response included placing adsorbent booms in the creek, excavating contaminated soil, removing oil-coated ice, and removing produced water from the creek. The electrical conductivity and chloride concentration in water along the creek, the Little Muddy River, and Missouri River were found to be elevated above background levels, as were samples taken from ground water recovery trenches.

More incidents from North Dakota are documented at the North Dakota Department of Health (NDDOH) Environmental Health web site (see <http://www.ndhealth.gov/EHS/Spills/>). For the period from November, 2012 to November 2013, NDDOH reported 552 releases of produced water which were retained within the boundaries of the production or exploration facility and 104 which were not (see http://www.ndhealth.gov/ehs/foia/spills/ChartWebPageOG_20121101_20131111.pdf).

7.7.2.2. Well Blowouts

Fingerprinting of water from two monitoring wells in Killdeer, ND, was used to determine that brine contamination in the two wells resulted from a well blowout during a hydraulic fracturing operation. Although the target formation was the Bakken Shale, data indicated that the residual signatures of the brine were characteristic of the overlying Madison limestone formation ([U.S. EPA, 2015j](#)). Prior research into out-of-zone hydraulic fracturing of the Bakken formation indicated that a large number of hydraulically fractured wells contain water that is external to the Bakken Zone ([Arkadakskiy and Rostron, 2013a](#); [Arkadakskiy and Rostron, 2012a](#); [Peterman et al., 2012](#)). The Bakken wells that contained external water were found to all contain water from the Mississippian Lodgepole formation (part of the Madison Group). The average volume of external water was 34% and the external water volume ranged from 10% to 100% ([Arkadakskiy and Rostron, 2013a](#)). Another example of a well blowout associated with a hydraulic fracturing operation occurred in Clearfield County, PA. The well blew out, resulting in an uncontrolled flow of approximately 35,000 gal (132,000 L) of brine and fracturing fluid, along with an unquantified amount of gas; some of the fluids reportedly reached a nearby stream ([Barnes, 2010](#)). The blowout occurred while

the company was drilling out the plugs used to isolate one fracture stage from another. An independent investigation found that the primary cause of the incident was that the only blowout preventer on the well had not been properly tested. In addition, the company did not have certified well control experts on hand or a written pressure control procedure ([Vittitow, 2010](#)). In North Dakota, a blowout preventer failed, causing a release of between 50 and 70 barrels per day (2,100 gal/day or 7,900 L/day and 2,940 gal/day or 11,000 L/day) of flowback and oil ([Reuters, 2014](#)). A 3-ft berm was placed around the well for containment. Frozen droplets of oil and water sprayed on a nearby frozen creek. Liquid flowing from the well was collected and trucked offsite. Multiple well communication events reported by the media have also led to flowback and produced water spills ranging from around 700 to 35,000 gal (2,600 L to 130,000 L) ([Vaidyanathan, 2013a](#)).

7.7.2.3. Leaks from Pits and Impoundments

Leaks of flowback and produced water from on-site pits and impoundments have caused releases as large as 57,000 gal (220,000 L) and have caused surface and ground water impacts ([Vaidyanathan, 2013b](#); [PBFC 2011](#); [PADEP 2010](#)). VOCs have been measured in groundwater near the Duncan Oil Field in New Mexico downgradient of an unlined pit storing produced water ([Sumi, 2004](#); [Eiceman, 1986](#)). Aspects of environmental transport from unlined pits are discussed below in Section 7.8.5.

Two of the EPA's retrospective case studies found potential impacts from produced water impoundments. In the southwest Pennsylvania case study ([U.S. EPA, 2015k](#)), elevated chloride concentrations and their timing relative to historical data suggested a recent ground water impact to a private water well occurred near an impoundment. The water quality trends suggested that the chloride anomaly was related to the impoundment, but site-specific data were not available to provide definitive assessment of the cause(s) and the longevity of the impact. Evaluation of other water quality parameters did not provide clear evidence of flowback or produced water impacts.

In the Wise County, TX case study ([U.S. EPA, 2015m](#)), impacts to two water wells were attributed to brine, but the data collected for the study were not sufficient to distinguish among four possible sources, one of which was leaks from reserve pits and/or impoundments. The others were: brine migrating from underlying formations along wellbores, brine migrating from underlying formations along natural fractures, and brine migrating from a nearby brine injection well. Alternate sources for the impacts were considered, including road salting, landfill leachate, septic tanks, and animal wastes, but evaluation of data showed that these were not likely. A third well experienced similar impacts, but a landfill leachate source could not be ruled out in that case. [Richter and Kreitler \(1993\)](#) reviewed sources of salinity to ground water resources by evaluating reviewing major sources, which included natural saline ground water, halite dissolution, sea-water intrusion, oil-field brine, agriculture, saline seeps and road salt. For each source [Richter and Kreitler \(1993\)](#) provided a state-by-state review of the potential occurrence, which can be used as a general guide to potential sources of salt at a specific area of interest.

7.7.2.4. Data Compilation Studies

Environmental impacts from hydraulic fracturing-related fluids have been explored to a limited extent in recent scientific literature ([Brantley et al., 2014](#); [Farag and Harper, 2014](#); [Gross et al.,](#)

2013; Olmstead et al., 2013; Papoulias and Velasco, 2013; Vidic et al., 2013; Considine et al., 2012; Rozell and Reaven, 2012).

From an Oklahoma Corporation Commission database of almost 13,000 releases reported from 1993 to 2003, Fisher and Sublette (2005) determined that the primary origins of produced water releases were leaks from lines, tanks, wellheads, with lesser numbers of releases from surface equipment, and pits. The most common cause was overflows followed by illegal activity, storms, fire accidents and corrosion. For these types of releases, the median release volume ranged from 20 bbl (840 gal or 3,180 L) to 60 bbl (2,500 gal or 9,500 L), and the maximums from 200 bbl (8,400 gal or 31,800 L) to 2,800 bbl (118,000 gal or 445,200 L).

As noted in Text Box 5-14 of Chapter 5, U.S. EPA (2015n) characterized hydraulic fracturing-related spills. Of the spills related to hydraulic fracturing activities (457 spills), 225 (49%) were spills of flowback and produced water. These spills were characterized with respect to volumes, spilled materials, sources, causes, environmental receptors, containment, and response. Most of the produced water spills in the EPA study occurred in Colorado (48%) and Pennsylvania (21%). Flowback and produced water constitute 84% (approximately 2.0 million gal or 7.6 million L) of the total volume of hydraulic fracturing-related spills as calculated from Appendix B of U.S. EPA (2015n).¹ Flowback and produced water spills were characterized by numerous low-volume spills; half of the spills with reported volumes were less than 1,000 gal (3,800 L), and few spills exceeded 10,000 gal (38,000 L). Of the volume of spilled flowback and produced water, 16% was recovered for on-site use or disposal, 76% was reported as unrecovered, and 8% was unknown. The potential impact of the unknown and unrecovered volume on drinking water resources is unknown.

Known sources for flowback and produced water spills include storage containers (e.g., pits, impoundments, or tanks), wells or wellheads, hoses or lines, and equipment. Storage containers accounted for 58% of flowback and produced water spills. The fewest spills occurred from wells and wellheads, but these spills had the greatest spill volumes compared to all other sources.

The causes of these spills were human error (38%), equipment failure (17%), failures of container integrity (13%), miscellaneous causes (e.g., well communication, well blowout), and unknown causes. Most of the volume spilled (74%), however, came from spills caused by a failure of container integrity.

In some of the cases, spills reached environmental receptors: soil (141 spills), surface water (17 spills), and ground water (1 spill); of these spills, 13 reached both soil and surface water. Consequently 146 unique produced water spills reached environmental receptors, accounting for 65% of the 225 cases and accounting for approximately 422,000 gal (1.60 million L) of flowback and produced water. Spills with known volumes that reached a surface water body ranged from

¹ Chemicals and products, fracturing fluid, fracturing water, equipment fluids, hydrocarbons, and unknown fluids constitute the additional 16% (approximately 360,000 gal or 1.4 million L) of the total volume of hydraulic fracturing-related spills as calculated from Appendix B of U.S. EPA (2015d).

less than 170 gal (640 L) to almost 74,000 gal (280,000 L). In 30 cases, it is unknown whether a spill of flowback and produced water reached an environmental receptor of any type.

[Gross et al. \(2013\)](#) analyzed the Colorado Oil and Gas Conservation Commission's database for ground water BTEX concentrations linked to hydraulic fracturing-related surface spills between July 2010 and July 2011 in Weld County, CO. Only spills with an impact on ground water were included in the study. The 77 reported spills accounted for less than 0.5% of nearly 18,000 active wells. Forty-six of the 77 spills consisted of produced water and oil. Of the remaining spills, 23 consisted of only oil and 8 consisted of only produced water. Thus the results that follow include cases with no produced water spill. From these composited spills, benzene concentrations in 90% of the ground water samples exceeded 5 µg/L, the U.S. drinking water standard. Additionally, 30% of toluene, 12% of ethylbenzene, and 8% of xylene sample concentrations exceeded 1 mg/L, 0.7 mg/L and 10 mg/L, respectively ([Gross et al., 2013](#)).

Based on five spills for which volumes were reported, the average volume of a produced water spill was 294 gal (1,110 L), ranging from 42 (160 L) to 1,176 gal (4,450 L) ([Gross et al., 2013](#)). Spill areas averaged 2,120 ft², with an average depth of 7 ft. Tank battery systems and production facilities were the biggest volume sources of spills with ground water impacts. Equipment failure was the most common cause of spills with ground water impacts. Shallow ground water within the study area (Niobrara Shale within the Denver-Julesburg Basin) is the main source of water for residents due to limited surface water availability. Of the 77 reported spills, secondary containment was absent from 51 of them ([Gross et al., 2013](#)).

As noted from the Colorado ([Gross et al., 2013](#)) and Oklahoma ([Fisher and Sublette, 2005](#)) studies, oil releases may occur alongside produced water spills. Review of recent oil field incidents in North Dakota also shows incidents with both produced water and oil releases (<http://www.ndhealth.gov/EHS/Spills/>). Oil releases are characterized by a number of features including their unique hydrocarbon composition and physical properties. Impacts can include: surface runoff, infiltration into soils, formation of sheens and oil slicks on surface waters, evaporation, oxidation, biodegradation, emulsion formation, and particle deposition ([U.S. EPA, 1999](#)).

A statistical analysis of oil and gas violations in Pennsylvania found that violations regarding structurally unsound impoundments or inadequate freeboard (vertical distance from the surface water level to the overflow elevation) were the second most frequent type of violation with 439 instances in the period from 2008 to 2010 ([Olawoyin et al., 2013](#)). In a study of pits and impoundments in West Virginia, [Ziemkiewicz et al. \(2014\)](#) found common problems of slope stability and liner deficiencies. Construction quality control and quality assurance were often inadequate; the authors found a lack of field compaction testing, use of improper types of soil, excessive slope lengths, buried debris, and insufficient erosion control ([Ziemkiewicz et al., 2014](#)).

[Brantley et al. \(2014\)](#) reviewed PA DEP's online oil and gas compliance database for notices of violation issued to companies developing unconventional gas resources. Between May 2009 and April 2013, 8 spills of flowback and produced water ranging from more than 4,000 gal (15,000 L) to

more than 57,000 gal (220,000 L) reached surface water resources. The spills typically resulted in local impacts to environmental receptors and required remediation and monitoring. However, the study indicated the likelihood of a leak or spill of hydraulic fracturing-related fluids was low (less than 1%, based on 32 large spills out of more than 4,000 complete wells). Due to lack of data, specific impacts to the eight receiving surface waters were not discussed, other than noting the produced water had contacted the surface water.

The [Brantley et al. \(2014\)](#) analysis of the PA DEP positive determination letters written in response to water-user complaints illustrates the importance of pre-drilling sampling, as it is one criterion that allows operators to refute the presumption that drilling caused water supply impacts (see Chapter 6). The importance of this pre-drilling sampling and analysis is highlighted by naturally occurring exceedances of EPA secondary MCLs for manganese and iron in private wells in Pennsylvania ([Boyer et al., 2011](#); [Williams et al., 1998](#)). [Boyer et al. \(2011\)](#) state that more than 40% of private water wells in Pennsylvania fail to meet federal drinking water standards. [Boyer et al. \(2011\)](#) analyzed pre-drilling samples from private water wells in northeastern and southwestern Pennsylvania and showed that 20% (of 222 wells) failed the drinking water standard for iron and 27% (of 203 wells) failed for manganese.¹ [Williams et al. \(1998\)](#), in their evaluation of over 200 wells in Bradford, Tioga, and Potter counties in northeastern Pennsylvania, indicate about 50% of the wells exceeded secondary MCLs for iron and manganese.² According to [Boyer et al. \(2011\)](#), higher concentrations of these constituents tend to be associated with the sodium chloride (Na-Cl) type ground water often found in valleys in zones of more restricted ground water flow (portions of aquifers with low permeability). Saline water can be found at shallow depths in these areas ([Williams et al., 1998](#)).

As an example of another set of criteria for assessing sites potentially contaminated by hydraulic fracturing activities, the EPA (2012f) developed an approach to study sites where the impacts to drinking water resources and the potential sources of the impacts are unknown, but may have been the object of water-user complaints. The approach is based on a tiered scheme where results from each tier are used to refine activities in higher tiers. The four tiers were as follows:

- Verify potential issue:
 - Evaluate existing data and information from operators, private citizens, state and local agencies, and tribes (as appropriate).
 - Conduct site visits.
 - Interview stakeholders and interested parties.
- Determine approach for detailed investigations:
 - Conduct initial sampling of water wells, taps, surface water and soils.

¹ Percentage of other parameters failing standards: 17% of 233 wells for pH, 3% of 233 wells for TDS, <1% of 226 wells for chloride, 1% of 218 wells for Barium, <1% of 177 wells for sulfate, 33% of 125 wells for coliforms, 4% of 115 wells for arsenic, 8% of 122 wells for fecal coliforms, 32% of 102 samples for turbidity.

² Naturally occurring constituents occasionally exceeding EPA primary MCLs in this area include barium, combined radium-226 and radium-228, and arsenic.

- Identify potential evidence of drinking water contamination.
- Develop conceptual site model describing possible sources and pathways of the reported or potential contamination.
- Develop, calibrate, and test fate and transport model(s).
- Conduct detailed investigations to detect and evaluate potential sources of contamination:
 - Conduct additional sampling of soils, aquifer, surface water, and produced water pits/tanks where present.
 - Conduct additional testing, including further water testing with new monitoring points, soil gas surveys, geophysical testing, well mechanical integrity testing, and stable isotope analyses.
 - Refine conceptual site model and further test exposure scenarios.
 - Refine fate and transport model(s) based on new data.
- Determine the source(s) of any impacts to drinking water resources:
 - Develop multiple lines of evidence to determine the source(s) of impacts to drinking water resources.
 - Exclude possible sources and pathways of the reported contamination.
 - Assess uncertainties associated with conclusions regarding the source(s) of impacts.

This tiered assessment strategy provides an outline for collecting data and evaluating lines of evidence for determining whether impacts have occurred.

7.7.3. Case Studies of Potentially Impacted Sites

7.7.3.1. Flowback and Produced Water Release from an Illegal Discharge Impacts Surface and Ground Water in Lycoming County, Pennsylvania

An estimated 6,300 gal to more than 57,000 gal (24,000 to 220,000 L) of Marcellus Shale produced water was illegally discharged at XTO Energy Inc.'s Marquardt pad and flowed into the Susquehanna River watershed in November 2010 ([U.S. EPA, 2013g](#)).¹ Overland and subsurface flow of released fluids affected proximal surface water, a subsurface spring, and soil. No impacts to drinking water wells and springs within 1 mile of the release were observed at the last sampling date (17 days post-spill). However, residual, soil-associated produced water constituents could reach drinking water resources in the future through surface runoff or infiltration to the ground water ([Science Applications International Corporation, 2010](#)). The release, which occurred at XTO's Marquardt 8537H well pad in Penn Township, Lycoming County, PA, was discovered after a routine inspection by the Pennsylvania Department of Environmental Protection. Subsequent investigation

¹ Violations associated with this incident can be found at the Pennsylvania Department of Environmental Protection's Oil and Gas Compliance Report database found at http://www.portal.state.pa.us/portal/server.pt/community/oil_and_gas_compliance_report/20299 under the following inspection IDs: 1928978, 1928992, and 1929005.

revealed that flowback and produced water had been discharging into surface waters for over two months after the fluid was released from multiple tanks with open or missing valves on November 16, 2010 ([U.S. EPA, 2013g](#)).

Geochemical characterization of this produced water indicated concentrations of barium, chloride, iron, manganese, and TDS above Pennsylvania's surface water quality standards, and above the statewide health standards for medium-specific concentrations (SHS MSCs) for ground water use in residential and nonresidential settings ([Science Applications International Corporation, 2010](#)). The produced water also contained elevated levels of bromide, calcium, sodium, and strontium, which lack state surface water quality standards and SHS MSCs ([Science Applications International Corporation, 2010](#)).

Post-spill surface water delineations indicated that released fluids migrated to an unnamed stream known as Tributary 19617. The released fluids migrated approximately 1,400 ft (427 m) overland to a depression which contains a natural fracture with a hydrological connection to a spring ([Schmidley and Smith, 2011](#)). The distance from the depression to the stream is approximately 600 ft (183 m). Released fluids also drained through surface soils into ground water, which was then released in seeps to the spring and stream; elevated levels of barium, bromide, calcium, chloride, sodium, strontium, and TDS resulted ([U.S. EPA, 2013g](#)). Elevated levels of these constituents, particularly barium, bromide, and strontium, were indicative of Marcellus Shale flowback and produced water that had mixed with surface water ([Brantley et al., 2014](#)). Barium and chloride were the only dissolved constituents detected in the stream that exceeded state surface water quality standards; the remaining constituents lack established state surface water quality standards.

Results from XTO's temporal study of surface water quality confirmed impacts to the stream from produced water. Surface water quality was characterized at the confluence of the stream and spring, and at the stream's upstream and downstream segments, for 65 days post-spill ([Science Applications International Corporation, 2010](#)). Downstream barium and bromide levels were one to two orders of magnitude greater than upstream levels through this period. In addition, stream strontium levels were two to three orders of magnitude greater than upstream levels at this time. Chloride was initially detected in the stream with concentrations exceeding state water quality standards ([Schmidley and Smith, 2011](#)). Average chloride concentrations for stream samples were two orders of magnitude greater than upstream concentrations ([PA DEP, 2011c](#)). By January 2011, stream chloride concentrations had dropped below the limit established by Pennsylvania's surface water quality standards.

Delineation of chloride concentrations within on-site soil indicated soil impacts due to overland flow of flowback and produced water ([Science Applications International Corporation, 2010](#)). Five hundred tons of affected soil was consequently excavated for off-site disposal. Chloride concentrations decreased with increased distance from the spill site but remained elevated above background levels even at distances of a few thousand feet ([Science Applications International Corporation, 2010](#)). Produced water constituents that were present in soil at concentrations above background levels (i.e., barium, sodium, strontium) could be available for long-term runoff and

infiltration. For instance, the continued presence of chloride in affected soils is likely due to precipitated chloride salts in soil pores from residual produced water ([Science Applications International Corporation, 2010](#)), which may leach later. Near-term sampling (up to 17 days after the spill) found no elevated constituents indicative of runoff or infiltration of produced water when XTO sampled 14 drinking water wells and springs within one mile of the well pad. XTO was ordered to create a storm water collection system for off-site disposal of impacted storm water and to establish on-site water monitoring wells to track long-term ground water quality between the well pad and the stream ([Schmidley and Smith, 2011](#)). Other cases of illegal dumping have been reported ([Caniglia, 2014](#); [U.S. EPA, 2013g](#); [Pattera, 2011](#)).

7.7.3.2. Flowback Fluid Reaches Towanda Creek Due to Well Blowout in Bradford County, Pennsylvania, Causing Short-Term Impacts

The Chesapeake Energy ATGAS 2H well, located in Leroy Township, Bradford County, PA, experienced a wellhead flange failure on April 19, 2011, during hydraulic fracturing operations. Approximately ten thousand gallons (38,000 L) of flowback fluids spilled into an unnamed tributary of Towanda Creek, a state-designated trout stock fishery and a tributary of the Susquehanna River ([USGS, 2013b](#); [SAIC and GES, 2011](#)). Chesapeake conducted post-spill surface and ground water monitoring ([SAIC and GES, 2011](#)). In addition, the EPA, PADEP, and Chesapeake collected split samples from seven private wells within the vicinity of the blowout. The EPA requested that the Agency for Toxic Substances and Disease Registry (ATSDR) evaluate the environmental data collected from seven private wells to determine whether harmful health effects would be expected from consuming or using the well water. Data from Pre-blowout private well samples, collected approximately six months prior to drilling activity at the site, were included in the evaluation.

Between the pre- and post-blowout samples, [ATSDR \(2013\)](#) determined that there was factor of ten increases in some analyte concentrations (methane, barium, calcium, chloride, magnesium, manganese, potassium, and sodium) and a factor of 7 increase in iron concentration in one well (RW04) near the site. Other wells showed elevated levels of certain analytes.¹ ATSDR concluded that although the available data *suggested* that the ground water near this site is impacted by gas activities, the data for RW04 did not conclusively indicate an impact. [ATSDR \(2013\)](#) concluded that further evaluation is needed to characterize any relationship between the drinking water wells and aquifers as a result of changes in site conditions. Further sampling would be required to determine current impacts, trends, and chronic exposures to ground water constituents related to natural gas activities.

¹ Elevated sodium levels were detected in 6 wells, levels in 5 of them (RW02, RW03, RW05, RW06, and RW07) may be of concern to sensitive subpopulations; while the last (RW04) would exceed the dietary guideline for both sensitive and the general population. ATSDR judged that elevated lithium concentration in two wells (RW04 and RW06) could be a concern to individuals undergoing lithium therapy. One well (RW02) showed elevated arsenic concentrations, but these were similar in the pre- and post-blowout samples. Gross alpha radiation levels were above the EPA maximum contaminant level in one well (RW03), and ATSDR did not expect adverse health effects from drinking this water. ATSDR did not expect adverse health effects for the user of five private wells (RW01, RW03, RW05, RW06 (excepting for possible lithium impacts) and RW07).

Chesapeake concluded that there were short-term impacts to surface waters of a farm pond within the vicinity of the well pad, the unnamed tributary, and Towanda Creek following the event (SAIC and GES, 2011). The lower 500 feet of the unnamed tributary exhibited elevated chloride, TDS, and specific conductance, which returned to background levels in under a week. Towanda Creek experienced these same elevations in concentration, but only at its confluence with the unnamed tributary; elevated chloride, TDS, and specific conductance returned to background levels the day after the blowout (SAIC and GES, 2011).

7.7.4. Roadway Transport of Produced Water

Accidents during transportation of hydraulic fracturing produced water are a possible mechanism leading to potential impacts to drinking water. Nationwide data are not available, however, on the number of such accidents that result in impacts. An estimate of releases from truck transport of produced water could be made as follows:

$$\text{Total number of truckloads} = \frac{\text{Total number of wells} \times \text{Produced water volume per well}}{\text{Produced water volume per truck}}$$

Then the total distance traveled by all trucks is given by:

$$\text{Total distance traveled} = \text{Total number of truckloads} \times \text{Distance per truck}$$

The number of crashes impacting drinking water resources can be estimated from:

$$\begin{aligned} \text{Total crashes impacting drinking water resources} \\ = \text{Fraction of crashes releasing waste that impacts drinking water resources} \\ \times \text{Fraction of all crashes releasing waste} \times \text{Crashes per distance} \end{aligned}$$

Estimates of all but one of the quantities in these calculations can be made from various literature sources, which are described in Appendix E. A key parameter is the number of crashes of trucks per distance traveled. In 2012, the U.S. Department of Transportation (DOT) estimated that the number of crashes per 100 million highway miles driven of a type of large truck was 110, which is a relatively small number. A key parameter that is unknown is the number of crashes which impact drinking water resources, so definitive estimates of impacts to drinking water resources cannot be made. Alternatively, as an upper bound on drinking water resource impacts, the number of crashes which release waste can be estimated. Based on various assumptions and scenarios presented in Appendix E, the number of crashes with releases is bounded by the low tens of events. At 20 m³ per truckload, the volumes are low relative to the typical volume of produced water.

Several limitations are inherent in this analysis, including differing rural road accident rates and highway rates, differing produced water endpoints, and differing amounts of produced water transported. Further, the estimates present an upper bound on impacts, because not all releases would reach or impact drinking water resources.

7.7.5. Studies of Environmental Transport of Released Produced Water

In this subsection, we describe transport study results that illustrate how produced waters have been shown to be transported from historical disposal practices and spills. Over the history of oil production in the U.S., produced water disposal methods have evolved from land application to storage in unlined ponds to deep well injection ([Whittemore, 2007](#)), although some unlined pits continue in use where allowed by states. The changes in practice occurred because of pollution impacts: first to surface waters and aquatic biota, and then to ground water from disposal ponds. Evaluation of sites contaminated by these historic practices sheds light on the potential for transport of released produced water, as discussed below.

Impacts to ground water might occur following a spill on land. When the liquid is highly saline, its migration is affected by its high density and viscosity compared with that of fresh water. When spilled flowback or produced water flows over land, a fraction of the liquid is subject to infiltration. The fraction depends on the rate of release, surface cover (i.e., pavement, cracked pavement, vegetation, bare soil, etc.), slope of the land surface, subsurface permeability, and the moisture content in the subsurface.

The potential for impacts from produced water spills depends on the distance from the source to receptor; the distance depends on local topography. One study investigated receptor distances on a formation basis ([Entrekin et al., 2011](#)). The distance between gas wells and drainage ways was determined to average 273 m (890 ft) for the Marcellus Shale and 353 m (1160 ft) for the Fayetteville Shale ([Entrekin et al., 2011](#)). Some wells were much closer, being as close as 1 m (3.28 ft). For one location in each formation a separate analysis gave a mean estimate of 153 m (500 ft) for the Marcellus Shale and 130 m (430 ft) for the Fayetteville Shale. The average distance to public drinking water intakes was 15 km (9.32 mi). The average distance to public water supply wells was 37 km (23.0 mi) for the Marcellus Shale and 123 km (76.4 mi) for the Fayetteville Shale. As the density of gas development increases the number of gas wells located close to drainage ways and public water supply wells may also increase.

For example, [Whittemore \(2007\)](#) described a site with relatively little infiltration due to moderate to low permeability of silty clay soil and low permeability of underlying shale units. Thus, most of the historically surface-disposed produced water at the site flowed into surface drainages. Observed historic levels of chloride in receiving waters resulted from the relative balance of produced water releases and precipitation runoff, with high concentrations corresponding to low stream flows. Persistent surface water chloride contamination was attributed to slow flushing and discharge of contaminated ground water.

Transport from the land surface to the water table is further characterized in general by flow through variably water-saturated media, preferential flow paths, fractures in clays, and macropores. Preferential flow paths along microscale heterogeneities are known to exist and dominate transport even after cycles of repeated drying and rewetting. The effect of flowback on transport of colloids has recently been evaluated in laboratory sand columns. The authors found that flowback increased the mobility of colloidal particles, which potentially serve as a source of aquifer contamination ([Sang et al., 2014](#)).

In another study, [Otton et al. \(2007\)](#) reported on a site in Oklahoma where two abandoned pits were major sources for releases of produced water and oil. Saline water from the pits flowed through thin soils and readily percolated into underlying permeable bedrock. Deeper, less permeable bedrock was contaminated by salt water later in the history of the site, presumably due to fractures ([Otton et al., 2007](#)). The mechanisms proposed were lateral movement through permeable sand bodies, vertical movement along shale fractures, and possibly increased permeability from clay flocculation and shrinkage due to the presence of highly saline water ([Otton et al., 2007](#)).

Because it is denser than freshwater, saline produced water can migrate downward through aquifers. [Whittemore \(2007\)](#) reported finding oilfield brine with a chloride concentration of 32,900 mg/L at the base of the High Plains aquifer. Where aquifers discharge to streams, saline stream water has been reported, although at reduced concentrations ([Whittemore, 2007](#)), likely due to diffusion within the aquifer and mixing with stream water. The stream flow rate, in part, determines mixing of substances in surface waters. High flows are related to lower chemical concentrations, and vice versa, as demonstrated for bromide by [States et al. \(2013\)](#) for the Allegheny River.

Generally, the deeper that brine can move into an aquifer, as impacted by the volume and timing of the release, the longer the duration of contamination ([Whittemore, 2007](#)). [Kharaka et al. \(2007\)](#) reported on studies at a site in Oklahoma with one abandoned and two active unlined brine pits. Produced water from these pits penetrated 3- to 7-m thick shale and siltstone units, creating three plumes of high-salinity water (5,000 to 30,000 mg/L TDS). The impact of these plumes on the receiving water body (Skiatook Lake) was judged to be minimal, although the estimate was based on a number of notably uncertain transport quantities ([Otton et al., 2007](#)).

Chloride impacts from produced water spills were studied through scenario modeling releases of 100 bbl (4,200 gal or 15,900 L) and 10,000 bbl (420,000 gal or 1.59 million L) ([API, 2005](#)). The scenarios included transport through a homogeneous or heterogeneous unsaturated zone using the HYDRUS-1D model ([Šimunek et al., 1998](#)) and mixing within the top portion of a shallow aquifer using a specially developed spreadsheet model. The results of the scenario modeling indicated that ground water quality is unlikely to be impaired for spills with small soil penetration depths, which correspond to spills distributed over large areas. Large spills of 100,000 bbl (4.2 million gal or 15.9 million L) over sandy unsaturated zones were found to have a high potential to impact ground water quality ([API, 2005](#)). Spills of less than 100 bbl (420 gal or 1,590 L) were not modeled and were presumed to have low impacts based on the results from the larger spills. The results were constrained by the underlying assumptions of HYDRUS-1D—that there were no preferential flow paths, including fractured systems, systems with macropores, or fine scale heterogeneities. More rapid and spatially extensive transport could occur in these settings.

7.7.6. Coalbed Methane

A CBM produced water impoundment in the Powder River Basin of Wyoming was studied for its impact on ground water ([Healy et al., 2011](#); [Healy et al., 2008](#)). Infiltration of water from the impoundment was found to create a perched water mound in the unsaturated zone above bedrock

in a location with historically little recharge. The subsurface sediments were found to be highly heterogeneous both physically and chemically, which increased the complexity of studying the site. Elevated concentrations of TDS, chloride, nitrate, and selenium were found at the site. For example, TDS exceeded 100,000 mg/L in one lysimeter sample, while the concentration was 2,275 mg/L in a composite CBM produced water sample (Healy et al., 2008). Most of the solutes found in the ground water mound did not originate with the CBM produced water, but rather were the consequence of dissolution of previously existing salts and minerals. The mechanisms were thought to be gypsum dissolution, cation exchange, and pyrite dissolution. Data from other sites indicated that the study site's ground water chemistry may not be typical and that the same phenomena may not occur at other sites in the basin (Healy et al., 2011).

7.7.7. Transport Properties

The identified constituents of flowback and produced water include inorganic chemicals in the form of cations and anions (including various types of metals, metalloids, and non-metals, and radioactive materials, among others) and organic chemicals, including identified compounds in various classes, and unidentified materials measured as TOC and DOC. Environmental transport of these chemicals depends on properties of the chemical and properties of the environment, and is extensively discussed in Section 5.8.3. In this section we discuss the characteristics of transport for inorganics and note that some inorganics may move with the water, while many of the others are influenced by reactions. For organic chemicals identified in produced water, we discuss EPI Suite™ estimates of the main transport parameters identified in Chapter 5, while noting the influences of salinity and temperature on these properties.

Transport of inorganic chemicals depends on the nature of ground water and vadose zone flow, and potential reactions among the inorganic chemical, solid surfaces, and geochemistry of the water. Some inorganic anions (i.e., chloride and bromide) move with their carrier liquid and are mostly impacted by physical transport mechanisms: flow of water and dispersion. In addition to the flow-related processes, transport of most inorganics is driven by three mechanisms related to partitioning to the solid phase: adsorption, absorption, and precipitation. The effects of these mechanisms depend on both chemical and environmental characteristics, including the surface reactivity, solubility, and redox sensitivity of the contaminant; and the type and abundance of reactive mineral phases, and the ground-water chemistry (U.S. EPA, 2007). Through the use of transport models, the effects of physical transport mechanisms and chemical processes are integrated. Examples of transport models for reactive metals include the Geochemist's Workbench (Bethke, 2014) and Hydrus (Šimunek et al., 1998).

Properties of organic chemicals which tend to affect the likelihood that a chemical will reach and impact drinking water resources if spilled include high chemical mobility in water, low volatility, and high persistence in water. Using the EPA chemical database EPI Suite™, we were able to obtain actual or estimated physicochemical properties for 86 of the 134 organic chemicals identified in produced water and listed in Appendix A. A portion of these, 66, are used in the chemical mixing stage (see Appendix Table C-8). EPI Suite™ results were generated for solubility, octanol water partition coefficient (K_{ow}), and the Henry's constant (see Figure 7-9). The log K_{ow} values are of the

identified organic chemicals skewed positively, indicating some of the chemicals have low mobility which may result in less extensive dissolved contaminant plumes in ground water. These compounds, however, have a higher tendency to sorb to particulate or colloidal materials and hence be transported in systems where particle transport is dominant, for example: colloid transport in ground water and sediment transport in surface water. The log Henry constant values tend to be below 0 indicating that at equilibrium the concentration in air is less than the concentration in water. This behavior is reflected in the log solubility plot, as the solubilities skew conversely toward high values.

The EPI Suite™ results are constrained by their applicability to one temperature (25 °C), and salinity (low). Temperature changes impact Henry's constant, K_{ow} , and solubility, and depend on the characteristics of the chemical and ions present (Borriukwisitsak et al., 2012; Schwarzenbach et al., 2002). In some cases the effect changes exponentially with salinity (Schwarzenbach et al., 2002). Therefore, property values that depart from the EPI Suite™ values are expected for produced water at elevated temperature and salinity.

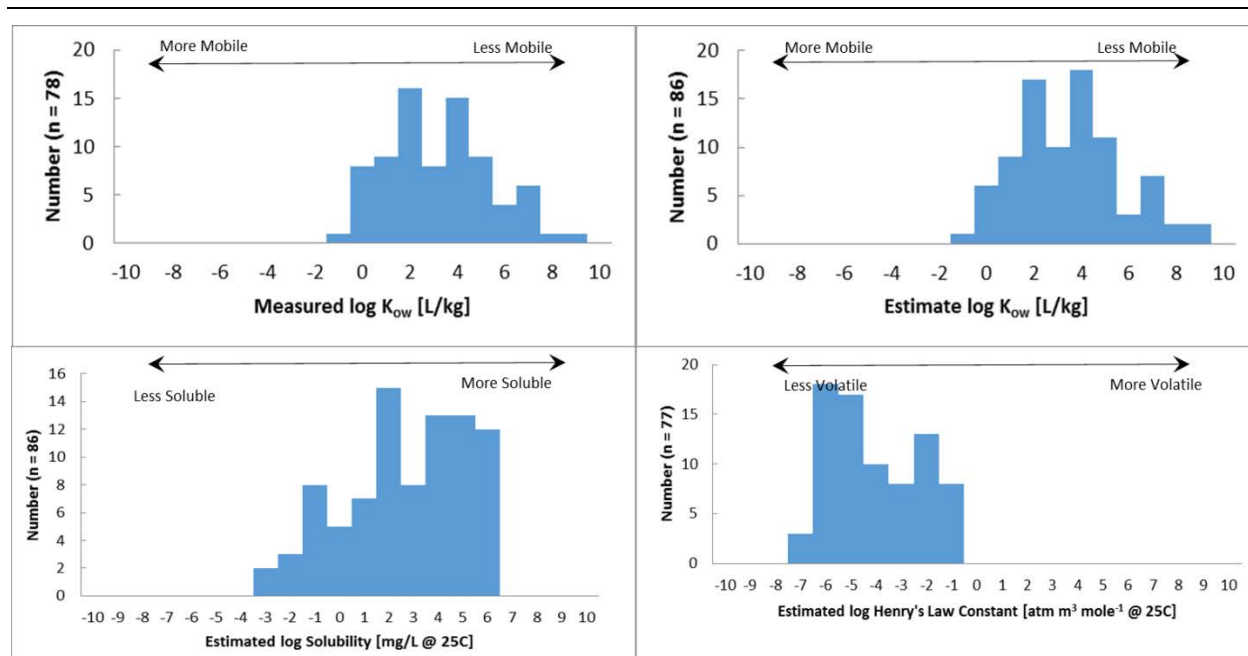


Figure 7-9. Histograms of physicochemical properties of 86 organic chemicals identified in produced water (physicochemical properties estimated by EPI Suite™).

7.8. Synthesis

After hydraulic fracturing is completed, the operator reduces injection pressure and water is allowed to flow back from the well to prepare for oil or gas production. The flowback water may contain fracturing fluid, fluid from the surrounding formation, and hydrocarbons. Initially this flowback is mostly fracturing fluid, but as time passes, the produced water becomes more similar to the water in the formation. This water is stored at the surface for eventual reuse or disposal.

Impacts to drinking water from flowback and produced water can occur if spilled flowback or produced water enters surface water bodies or aquifers.

7.8.1. Summary of Findings

The volume and composition of flowback and produced water vary geographically, both within and between different formations with time and with other site-specific factors. High initial rates of flowback decrease as time continues. The amount of fracturing fluid returned to the surface varies, and typically averages 10% to 25%. In most cases, lower flow rates of produced water continue throughout gas production.¹ In some formations (i.e., the Barnett Shale), the ultimate volume of produced water can exceed the volume of hydraulic fracturing fluid because of inflow of water.

The composition of flowback changes with time as the hydraulic fracturing fluid contacts the formation and mixes with the formation water. At the same time, reactions occur between the constituents of the fracturing fluid and the formation. Although varying within and between formations, shale and tight gas produced water typically contains high levels of TDS (salinity) and associated ionic constituents (bromide, calcium, chloride, iron, potassium, manganese, and sodium). Produced water may contain toxic materials, including barium, cadmium, chromium, lead, mercury, nitrate, selenium, and BTEX. CBM produced water can have lower levels of salinity if its coal source was deposited under freshwater conditions.

Flowback and produced water spills are known to have occurred across the country. The causes identified for these spills are container and equipment failures, human error, well communication, blowouts, pipeline leaks, and illegal dumping. Spills due to trucking accidents are possible, but accident rates in the United States suggest only a small number of such releases occur.

USGS studies of impacts of produced water disposal in unlined pits document the potential for surface releases (in these cases over multiple years) that have led to ground water impacts. Contaminant plumes can be traced to high TDS water disposed of in the pits, or geochemical reaction between infiltrating low-TDS water, in the case of CBM produced water, releasing existing minerals from the unsaturated zone to ground water.

7.8.2. Factors Affecting the Frequency or Severity of Impacts

The potential of spills of flowback and produced water to affect drinking water resources depends upon the release volume, duration, and composition. Larger spills of greater duration are more likely to reach a nearby drinking water resource than are smaller spills. The composition of the spilled fluid will also impact the severity of a spill, as certain constituents are more likely to affect the quality of a drinking water resource. Low-volume and short-duration spills are less likely to cause impacts, (see Section 7.7.5).

Potential impacts to water resources from hydraulic fracturing-related spills are expected to be affected by watershed and water body characteristics. For example, overland flow is affected by surface topography and surface cover. Infiltration of spilled produced water reduces the amount of

¹ Note that increasing produced water flow rates are indicative of water breakthrough and declining oil production.

water threatening surface water bodies. However, infiltration through soil may lead to ground water impacts. Produced water with lower constituent concentrations may produce lesser impacts, but the USGS studies of CBM produced water impoundments described in section 7.7.5 showed impacts caused by CBM water mobilizing existing minerals. The USGS studies on historical disposal of saline produced water in unlined pits detected ground water plumes discharging into surface water bodies. The potential impact to drinking water in such cases depends on the location of drinking water wells and the size of any surface water supply reservoir.

7.8.3. Uncertainties

We first discuss data gaps in our overall knowledge of flowback and produced water; closing such gaps would enable us to better predict impacts on drinking water resources. Second, we present uncertainties that, based on site-specific conditions, also affect our ability to determine potential impacts.

7.8.3.1. General Data Gaps

Knowledge of volume and some compositional aspects of flowback and produced water are known from published sources. Most of the available data on TENORM has come from the Marcellus Shale, where these are typically high in comparison to the limited data available from other formations. Only a few studies have attempted to sample and characterize the organic fraction of flowback and produced water; some data are available for shale and CBM, but none are available for tight formations. The reported organic chemical data from flowback likely does not capture the full range of chemicals that may be present, either as original components of the hydraulic fracturing solution or transformation products generated in the subsurface.

Characterization of produced water organics is limited by several factors. Development or use of proper analytical procedures depends upon knowing the identities of injected chemicals. Because the formulation of hydraulic fracturing fluids can contain proprietary chemicals, the exact formulations are not available. In addition, subsurface transformations yield degradation products, which themselves must have appropriate analytical methods. Further difficulties are due to matrix interference from high-TDS produced water. These problems result in the need to develop new methods for analyzing both organics and inorganics in produced water.

Nationwide data on spills of flowback and produced water are limited in two primary ways: the completeness of reported data cannot be determined, and individual states' reporting requirements differ ([U.S. EPA, 2015n](#)). Despite various studies, the total number of spills occurring in the United States, their release volumes and associated concentrations, can only be roughly estimated because of underlying data limitations.

7.8.3.2. Uncertainties at Individual Spill Sites

Spills of flowback and produced water present many uncertainties that, in combination, limit our ability to predict impacts on drinking water resources. Spills vary in volume, duration, and composition. The spilled liquid could be fracturing fluid mixed with formation water in a proportion that depends on the time that has passed since fracturing. As described in Section 7.7, spills may originate from blowouts, well communication, aboveground or underground pipeline

breaks, leaking impoundments, failed containers, human error (including illegal activities, failure to detect spills, and failure to report spills) or unknown causes. The difference between these causes affect the size and location of the spill. In addition, the factors governing transport of spilled fluid to a potential receptor vary by site: the presence and quality of secondary or emergency containment and spill response; the rate of overland flow and infiltration; the distance to a surface water body or drinking water well; and transport and fate processes. Impacts to drinking water resources from spills of flowback and produced water depend on environmental transport parameters, which can in principle be determined but are unlikely to be known or adequately specified in advance of a spill.

Because some constituents of flowback and produced water are constituents of natural waters (e.g., bromide in coastal surface waters) or can be released into the environment by other pollution events (e.g., benzene from gasoline releases, or bromide from coal mine drainage), baseline sampling prior to impacts is one way to increase certainty of an impact determination. Further sampling and investigation may be used to develop the linkage between a release and a documented drinking water impact. Produced water spill response typically includes delineation of the extent of oiled soils, sheens on water surfaces, and the extent of saline water. Extensive characterization of produced water is typically not part of spill response, and therefore the chemicals, and their concentrations, potentially impacting drinking water resources are not usually known.

7.8.4. Conclusions

Flowback and produced water has the potential to affect the quality of drinking water resources if it enters into a surface or ground water body used as a drinking water resource. This can occur through spills at well pads, or during transport of flowback. Specific impacts depend upon the spill itself, the environmental conditions surrounding the spill, water body and watershed characteristics, and the composition of the spilled fluid. Flowback and produced water may contain toxic constituents and can potentially render water unpalatable or unsafe to drink. Conclusive determination of impacts to water resources depends on commitment of resources to the implementation of sampling, analysis and evaluation strategies

Text Box 7-1. Research Questions Revisited.

What is currently known about the frequency, severity, and causes of spills of flowback and produced water?

- Surface spills of flowback and produced water from unconventional oil and gas production have occurred across the country. Some produced water spills have affected drinking water resources, including a few private drinking water wells. The majority of flowback and produced water spills are under 1,000 gallons. The causes identified for these are container and equipment failures, human error, well communication, blowouts, pipeline leaks, and illegal dumping.

What is the composition of hydraulic fracturing flowback and produced water, and what factors might influence this composition?

- The composition of flowback and produced water must be determined through sampling and analysis, both of which have limitations. The former due to the ability to access through production equipment and the latter due to issues with identifying target analytes in advance of analysis and the existence of appropriate analytical methods.
- The geochemical content of water flowing back initially reflects injected fluids. After initial flowback, returning fluid geochemistry shifts to reflect the geochemistry of formation waters and formation solids.
- According to available literature and data, conventional and unconventional flowback and produced water content are often similar with respect to the occurrence and concentration of many constituents.
- The least statistical variability in produced water content is exhibited between shale gas and tight gas produced water, and the most statistical variability is exhibited between shale gas and coalbed methane produced water.
- Much produced water is generally characterized as saline (with the exception of most coalbed methane produced water) and enriched in major anions, cations, metals, naturally occurring radionuclides, and organics.
- Shale and coalbed produced water is enriched in benzene. Benzene is a constituent of concern in Marcellus Shale, Raton CBM, and San Juan CBM produced water. Shale produced water is more likely to contain elevated average total BTEX levels than other unconventional produced water.
- Typically, unconventional produced water contains low levels of heavy metals. Elevated strontium and barium levels, however, are characteristic of Marcellus Shale flowback and produced water. CBM and, in particular, shale produced water are likely to contain NORM levels of concern.
- Composition data were limited. Most of the available data on produced water content were for shale formations and CBM basins, while little data were available for sandstone formations. Additionally, the majority of data were for inorganics, and little data were available for organics. Many more organic chemicals have been reported to have been used in hydraulic fracturing fluid than have been identified in produced water. The difference may be due to analytical limitations, limited study scopes, and undocumented subsurface reactions.
- Hydraulic fracturing flowback and produced water composition is influenced by the composition of injected hydraulic fracturing fluids, the targeted geological formation and associated hydrocarbon products, the stratigraphic environment, and subsurface processes and residence time.
- Spatial variability of produced water content occurs between plays of different rock sources (e.g., coal vs. sandstone), between plays of the same rock type (e.g., Barnett Shale vs. Bakken Shale), and within formations of the same source rock (e.g., northeastern vs. southwestern Marcellus Shale).

What are the chemical and physical properties of hydraulic fracturing flowback and produced water constituents?

- The identified constituents of flowback and produced water include inorganic chemicals (cations and anions in the form of metals, metalloids, non-metals, and radioactive materials), organic chemicals and compounds, and unidentified materials measured as TOC (total organic carbon) and DOC (dissolved organic carbon). Some constituents are readily transported with water (i.e., chloride and bromide), while others depend strongly on the geochemical conditions in the receiving water body (i.e., radium and barium), and assessment of their transport is based on site-specific factors. Using the EPA chemical

database EPI Suite, we were able to obtain actual or estimated physicochemical properties for 86 (64%) of the 134 chemicals identified in produced water.

- As in the case of chemicals in hydraulic fracturing fluid, chemical properties that affect the likelihood of an organic chemical in produced water reaching and impact drinking water resources in the short-term, include: high chemical mobility in water, low volatility, and high persistence in water. In general, EPI suite results suggest that organic chemicals in produced water tend toward lower mobility in water. Consequently these chemicals could remain in soils or sediments nearby spills. Low mobility may result in smaller dissolved contaminant plumes in ground water. Although these compounds are more likely to be transported associated with sediments in surface water or small particles in ground water. Organic chemical properties vary with salinity and the effects depend on the nature of the chemical.

If spills occur, how might hydraulic fracturing flowback and produced water contaminate drinking water resources?

- Spills of flowback or produced water might impact drinking water resources if the spill or release is of sufficient volume and duration, to reach the resource at a sufficient concentration. Impacts to in-use drinking water depend on proximity to sources. Scientific literature and published reports have shown that produced water spills have impacted drinking water resources.

7.9. References for Chapter 7

Ali, SA; Clark, WJ; Moore, WR; Dribus, JR. (2010). Diagenesis and reservoir quality. *Oilfield Rev* 22: 14-27.

Alley, B; Beebe, A; Rodgers, J; Castle, JW. (2011). Chemical and physical characterization of produced waters from conventional and unconventional fossil fuel resources. *Chemosphere* 85: 74-82.
<http://dx.doi.org/10.1016/j.chemosphere.2011.05.043>

API (American Petroleum Institute). (2005). Modeling study of produced water release scenarios. (Publication Number 4734). Washington, D.C.: API Publishing Services.
http://www.api.org/~media/files/ehs/environmental_performance/4734.pdf?la=en

API (American Petroleum Institute). (2010b). Water management associated with hydraulic fracturing. Washington, D.C.: API Publishing Services.
http://www.api.org/~media/Files/Policy/Exploration/HF2_e1.pdf

Arkadakskiy, S.; Rostron, BJ. (2012a). Stable isotope geochemistry helps in reducing out-of-zone hydraulic fracturing and unwanted brine production from the Bakken Reservoir. Available online at
http://isobrine.com/wp-content/uploads/2013/04/Arkadakskiy_Rostron_20121.pdf

Arkadakskiy, S; Rostron, B. (2013a). Tracking out-of-zone hydraulic fracturing in the Bakken with naturally occurring tracers. Paper presented at GeoConvention 2013: Integration Canadian Society of Petroleum Geologists, May 6-10, 2013, Calgary, AB, Canada.

Arthur, JD; Bohm, B; Coughlin, BJ; Layne, M. (2009b). Evaluating the environmental implications of hydraulic fracturing in shale gas reservoirs. Paper presented at SPE Americas E&P Environmental and Safety Conference, March 23-25, 2009, San Antonio, TX.

ATSDR (Agency for Toxic Substances and Disease Registry). (2005). Public health assessment guidance manual (Update). Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.
<http://www.atsdr.cdc.gov/hac/PHAManual/toc.html>

- ATSDR (Agency for Toxic Substances and Disease Registry). (2013). Health consultation: Chesapeake ATGAS 2H well site, Leroy Hill Road, Leroy, Leroy Township, Bradford County, PA. Atlanta, GA: ATSDR, Division of Community Health Investigations.
http://www.atsdr.cdc.gov/HAC/pha/ChesapeakeATGASWellSite/ChesapeakeATGASWellSiteHC10282013_508.pdf
- AWWA (American Water Works Association). (2013). Water and hydraulic fracturing: A white paper from the American Water Works Association. Denver, CO.
<http://www.awwa.org/Portals/0/files/legreg/documents/AWWAFrackingReport.pdf>
- Barbot, E; Vidic, NS; Gregory, KB; Vidic, RD. (2013). Spatial and temporal correlation of water quality parameters of produced waters from Devonian-age shale following hydraulic fracturing. *Environ Sci Technol* 47: 2562-2569.
- Barnes, T. (2010). 2 drillers fined for Pennsylvania gas well blowout. Available online at <http://www.post-gazette.com/news/environment/2010/07/14/2-drillers-fined-for-Pennsylvania-gas-well-blowout/stories/201007140241> (accessed March 3, 2015).
- Benko, KL; Drewes, JE. (2008). Produced water in the Western United States: Geographical distribution, occurrence, and composition. *Environ Eng Sci* 25: 239-246.
- Bethke, CM, ; Yeakel, S. (2014). The geochemists workbench. Release 10.0. *GWB essentials guide* (Version Release 10.0). Champaign, IL: Aqueous Solutions, LLC. Retrieved from
<http://www.gwb.com/pdf/GWB10/GWBessentials.pdf>
- Bibby, KI; Brantley, SL; Reible, DD; Linden, KG; Mouser, PJ; Gregory, KB; Ellis, BR; Vidic, RD. (2013). Suggested reporting parameters for investigations of wastewater from unconventional shale gas extraction. *Environ Sci Technol* 47: 13220-13221. <http://dx.doi.org/10.1021/es404960z>
- Blauch, ME; Myers, RR; Moore, TR; Lipinski, BA. (2009). Marcellus shale post-frac flowback waters - where is all the salt coming from and what are the implications? In *Proceedings of the SPE Eastern Regional Meeting*. Richardson, TX: Society of Petroleum Engineers.
- Blondes, MS; Gans, KD; Thordsen, JJ; Reidy, ME; Thomas, B; Engle, MA; Kharaka, YK; Rowan, EL. (2014). Data: U.S. Geological Survey National Produced Waters Geochemical Database v2.0 (Provisional) [Database]: U.S. Geological Survey :: USGS. Retrieved from
<http://energy.usgs.gov/EnvironmentalAspects/EnvironmentalAspectsofEnergyProductionandUse/ProducedWaters.aspx#3822349-data>
- Borrirukwisitsak, S; Keenan, HE; Gauchotte-Lindsay, C. (2012). Effects of salinity, pH and temperature on the octanol-water partition coefficient of bisphenol A. *IJESD* 3: 460-464.
<http://dx.doi.org/10.7763/IJESD.2012.V3.267>
- Boschee, P. (2014). Produced and flowback water recycling and reuse: Economics, limitations, and technology. *Oil and Gas Facilities* 3: 16-22.
- Bouska, V. (1981). *Geochemistry of coal*. New York, NY: Elsevier.
- Boyer, EW; Swistock, BR; Clark, J; Madden, M; Rizzo, DE. (2011). The impact of Marcellus gas drilling on rural drinking water supplies. Harrisburg, PA: The Center for Rural Pennsylvania.
<http://www.iogawv.com/Resources/Docs/Marcellus-drinking-water-2011.pdf>
- Brantley, SL; Yoxtheimer, D; Arjmand, S; Grieve, P; Vidic, R; Pollak, J; Llewellyn, GT; Abad, J; Simon, C. (2014). Water resource impacts during unconventional shale gas development: The Pennsylvania experience. *Int J Coal Geol* 126: 140-156. <http://dx.doi.org/10.1016/j.coal.2013.12.017>
- Breit, GN. (2002). USGS Produced waters database. Available online at
<http://energy.cr.usgs.gov/prov/prodwat/>
- Brinck, EL; Frost, CD. (2007). Detecting infiltration and impacts of introduced water using strontium isotopes. *Ground Water* 45: 554-568. <http://dx.doi.org/10.1111/j.1745-6584.2007.00345.x>

- Byrnes, AP. (2011). Role of induced and natural imbibition in frac fluid transport and fate in gas shales. Presentation presented at Technical Workshops for Hydraulic Fracturing Study: Fate & Transport, March 28-29, 2011, Arlington, VA.
- Caniglia, J. (2014). Youngstown contractor sentenced to 28 months for dumping fracking waste. Available online at http://www.cleveland.com/court-justice/index.ssf/2014/08/youngstown_contractor_sentence.html (accessed March 12, 2015).
- Chapman, EC; Capo, RC; Stewart, BW; Kirby, CS; Hammack, RW; Schroeder, KT; Edenborn, HM. (2012). Geochemical and strontium isotope characterization of produced waters from Marcellus Shale natural gas extraction. *Environ Sci Technol* 46: 3545-3553.
- Clark, CE; Horner, RM; Harto, CB. (2013). Life Cycle Water Consumption for Shale Gas and Conventional Natural Gas. *Environ Sci Technol* 47: 11829-11836. <http://dx.doi.org/10.1021/es4013855>
- Cluff, M; Hartsock, A; Macrae, J; Carter, K; Mouser, PJ. (2014). Temporal changes in microbial ecology and geochemistry in produced water from hydraulically fractured Marcellus Shale Gas Wells. *Environ Sci Technol* 48: 6508-6517. <http://dx.doi.org/10.1021/es501173p>
- Coleman, N. (2011). Produced formation water sample results from shale plays. Presentation presented at Technical Workshops for the Hydraulic Fracturing Study: Chemical & Analytical Methods, February 24-25, 2011, Arlington, VA.
- Considine, T; Watson, R; Considine, N; and Martin, J. (2012). Environmental impacts during Marcellus shale gas drilling: Causes, impacts, and remedies. (Report 2012-1). Buffalo, NY: Shale Resources and Society Institute. <http://cce.cornell.edu/EnergyClimateChange/NaturalGasDev/Documents/UBSRSI-Environmental%20Impact%20Report%202012.pdf>
- Dahm, KG; Guerra, KL; Xu, P; Drewes, JE. (2011). Composite geochemical database for coalbed methane produced water quality in the Rocky Mountain region. *Environ Sci Technol* 45: 7655-7663. <http://dx.doi.org/10.1021/es201021n>
- Dake, LP. (1978). Fundamentals of reservoir engineering. Boston, MA: Elsevier. <http://www.ing.unp.edu.ar/asignaturas/reservorios/Fundamentals%20of%20Reservoir%20Engineering%20%28L.P.%20Dake%29.pdf>
- Davis, JP; Struchtemeyer, CG; Elshahed, MS. (2012). Bacterial communities associated with production facilities of two newly drilled thermogenic natural gas wells in the Barnett Shale (Texas, USA). *Microb Ecol* 64: 942-954. <http://dx.doi.org/10.1007/s00248-012-0073-3>
- DeArmond, PD; DiGoregorio, AL. (2013a). Characterization of liquid chromatography-tandem mass spectrometry method for the determination of acrylamide in complex environmental samples. *Anal Bioanal Chem* 405: 4159-4166. <http://dx.doi.org/10.1007/s00216-013-6822-4>
- DeArmond, PD; DiGoregorio, AL. (2013b). Rapid liquid chromatography-tandem mass spectrometry-based method for the analysis of alcohol ethoxylates and alkylphenol ethoxylates in environmental samples. *J Chromatogr A* 1305: 154-163. <http://dx.doi.org/10.1016/j.chroma.2013.07.017>
- Demorest, DL; Wallace, ES. (1992). Radiochemical determination of norm in produced water utilizing wet chemistry separation followed by radiochemical analysis. In JP Ray; Engelhardt; Fr (Eds.), *Produced water: Technological/environmental issues and solutions* (pp. 257-266). New York, NY: Plenum Press. http://dx.doi.org/10.1007/978-1-4615-2902-6_21
- DOE (U.S. Department of Energy). (2004). A white paper describing produced water from production of crude oil, natural gas, and coal bed methane. Lemont, IL: Argonne National Laboratory. http://seca.doe.gov/technologies/oil-gas/publications/oil_pubs/prodwaterpaper.pdf
- DOE (U.S. Department of Energy). (2011a). A comparative study of the Mississippian Barnett shale, Fort Worth basin, and Devonian Marcellus shale, Appalachian basin. (DOE/NETL-2011/1478). <http://www.netl.doe.gov/technologies/oil-gas/publications/brochures/DOE-NETL-2011-1478%20Marcellus-Barnett.pdf>

- Dresel, PE; Rose, AW. (2010). Chemistry and origin of oil and gas well brines in western Pennsylvania (pp. 48). (Open-File Report OFOG 1001.0). Harrisburg, PA: Pennsylvania Geological Survey, 4th ser. <http://www.marcellus.psu.edu/resources/PDFs/brines.pdf>
- EERC (Energy and Environmental Research Center, University of North Dakota). (2013). BakkenSmart: water [Fact Sheet]. Grand Forks, ND: Energy and Environmental Research Center. <http://www.undeerc.org/bakken/pdfs/NDIC-NDPC-Water-Fact-Sheet.pdf>
- Eiceman, GA. (1986). Hazardous organic wastes from natural gas production, processing and distribution: Environmental fates. (WRRRI report, no. 227). New Mexico: Water Resources Research Institute. <http://wrri.nmsu.edu/publish/techrpt/abstracts/abs227.html>
- Engelder, T. (2012). Capillary tension and imbibition sequester frack fluid in Marcellus gas shale [Letter]. PNAS 109: E3625; author reply E3626. <http://dx.doi.org/10.1073/pnas.1216133110>
- Engle, MA; Rowan, EL. (2014). Geochemical evolution of produced waters from hydraulic fracturing of the Marcellus Shale, northern Appalachian Basin: A multivariate compositional data analysis approach. Int J Coal Geol 126: 45-56. <http://dx.doi.org/10.1016/j.coal.2013.11.010>
- Entrekin, S; Evans-White, M; Johnson, B; Hagenbuch, E. (2011). Rapid expansion of natural gas development poses a threat to surface waters. Front Ecol Environ 9: 503-511. <http://dx.doi.org/10.1890/110053>
- ESN Rocky Mountain (Environmental Services Network Rocky Mountain). (2003). Produced gas and water testing of CBM gas wells in the Raton Basin. Golden, CO. https://cogcc.state.co.us/Library/RatonBasin/ESN%20Final_Report.pdf
- Farag, AM; Harper, DD. (2014). A review of environmental impacts of salts from produced waters on aquatic resources. Int J Coal Geol 126: 157-161. <http://dx.doi.org/10.1016/j.coal.2013.12.006>
- Fertl, WH; Chilingar, GV. (1988). Total organic carbon content determined from well logs. SPE Formation Evaluation 3: 407-419. <http://dx.doi.org/10.2118/15612-PA>
- Fisher, JB; Sublette, KL. (2005). Environmental releases from exploration and production operations in Oklahoma: Type, volume, causes, and prevention. Environmental Geosciences 12: 89-99. <http://dx.doi.org/10.1306/eg.11160404039>
- Fisher, RS. (1998). Geologic and geochemical controls on naturally occurring radioactive materials (NORM) in produced water from oil, gas, and geothermal operations. Environmental Geosciences 5: 139-150. <http://dx.doi.org/10.1046/j.1526-0984.1998.08018.x>
- Gilmore, K; Hupp, R; Glathar, J. (2013). Transport of Hydraulic Fracturing Water and Wastes in the Susquehanna River Basin, Pennsylvania. J Environ Eng 140: B4013002. [http://dx.doi.org/10.1061/\(ASCE\)EE.1943-7870.0000810](http://dx.doi.org/10.1061/(ASCE)EE.1943-7870.0000810)
- Gregory, KB; Vidic, RD; Dzombak, DA. (2011). Water management challenges associated with the production of shale gas by hydraulic fracturing. Elements 7: 181-186.
- Gross, SA; Avens, HJ; Banducci, AM; Sahmel, J; Panko, JM; Tvermoes, BE. (2013). Analysis of BTEX groundwater concentrations from surface spills associated with hydraulic fracturing operations. J Air Waste Manag Assoc 63: 424-432. <http://dx.doi.org/10.1080/10962247.2012.759166>
- Guerra, K; Dahm, K; Dunderf, S. (2011). Oil and gas produced water management and beneficial use in the western United States. (Science and Technology Program Report No. 157). Denver, CO: U.S. Department of the Interior Bureau of Reclamation.
- GWPC and ALL Consulting (Ground Water Protection Council (GWPC) and ALL Consulting). (2009). Modern shale gas development in the United States: A primer. (DE-FG26-04NT15455). Washington, DC: U.S. Department of Energy, Office of Fossil Energy and National Energy Technology Laboratory. <http://www.gwpc.org/sites/default/files/Shale%20Gas%20Primer%202009.pdf>

- GWPC and IOGCC (Ground Water Protection Council and Interstate Oil and Gas Compact Commission). (2014). Fracturing fluid management. Available online at <http://fracfocus.org/hydraulic-fracturing-how-it-works/drilling-risks-safeguards> (accessed December 12, 2014).
- Haluszczak, LO; Rose, AW; Kump, LR. (2013). Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA. *Appl Geochem* 28: 55-61. <http://dx.doi.org/10.1016/j.apgeochem.2012.10.002>
- Hansen, E; Mulvaney, D; Betcher, M. (2013). Water resource reporting and water footprint from Marcellus Shale development in West Virginia and Pennsylvania. Durango, CO: Earthworks Oil & Gas Accountability Project. http://www.downstreamstrategies.com/documents/reports_publication/marcellus_wv_pa.pdf
- Hayes, T. (2009). Sampling and analysis of water streams associated with the development of Marcellus shale gas. Des Plaines, IL: Marcellus Shale Coalition. <http://eidmarcellus.org/wp-content/uploads/2012/11/MSCCommission-Report.pdf>
- Hayes, T. (2011). Characterization of Marcellus and Barnett shale flowback waters and technology development for water reuse. Paper presented at Hydraulic Fracturing Study: March 2011 Technical Workshop on Water Resource Management, March 29-30, 2011, Arlington, VA.
- Hayes, T; Severin, B. (2012a). Characterization of flowback water from the the Marcellus and the Barnett shale regions. Barnett and Appalachian shale water management and reuse technologies. (08122-05.09; Contract 08122-05). Hayes, T; Severin, B. http://www.rpsea.org/media/files/project/2146b3a0/08122-05-RT-Characterization_Flowback_Waters_Marcellus_Barnett_Shale_Regions-03-20-12.pdf
- He, Z. (2011). Flow of gas and water in hydraulically fractured shale gas reservoirs. EPA HF Workshop, March 28-29, 2011, Arlington, VA.
- Healy, RW; Bartos, TT; Rice, CA; Mckinley, MP; Smith, BD. (2011). Groundwater chemistry near an impoundment for produced water, Powder River Basin, Wyoming, USA. *J Hydrol* 403: 37-48. <http://dx.doi.org/10.1016/j.jhydrol.2011.03.042>
- Healy, RW; Rice, CA; Bartos, TT; Mckinley, MP. (2008). Infiltration from an impoundment for coal-bed natural gas, Powder River Basin, Wyoming: Evolution of water and sediment chemistry. *Water Resour Res* 44: n/a-n/a. <http://dx.doi.org/10.1029/2007wr006396>
- Horse, CA. (1981). Depositional environments of the Pennsylvanian Pottsville Formation in the Black Warrior Basin of Alabama. *Journal of Sedimentary Research* 51: 799-806. <http://dx.doi.org/10.1306/212F7DB5-2B24-11D7-8648000102C1865D>
- Hunter, JA; Moser, PH. (1990). Ground water availability in Jefferson County, Alabama: geological survey special map 224. Tuscaloosa, AL: Geological Survey of Alabama. http://www.ogb.state.al.us/documents/pubs/onlinepubs/Special_Maps/SM224_.PDF
- IUPAC (International Union of Pure and Applied Chemistry). (2014). Gold Book: matrix effect. Available online at <http://goldbook.iupac.org/M03759.html> (accessed April 8, 2015).
- Kharaka, YK; Kakouros, E; Thordsen, JJ; Ambats, G; Abbott, MM. (2007). Fate and groundwater impacts of produced water releases at OSPER B site, Osage County, Oklahoma. *Appl Geochem* 22: 2164-2176. <http://dx.doi.org/10.1016/j.apgeochem.2007.04.005>
- Langmuir, D; Riese, AC. (1985). THE THERMODYNAMIC PROPERTIES OF RADIUM. *Geochim Cosmo Acta* 49: 1593-1601.
- Lee, K; Neff, J. (2011). Produced water: Environmental risks and advances in mitigation technologies. New York, NY: Springer. <http://dx.doi.org/10.1007/978-1-4614-0046-2>
- Levis, E. (2011). Texas company pays \$93,710 settlement for polluting Clearfield County Creek. Pennsylvania Fish and Boat Commission. <https://www.fish.state.pa.us/newsreleases/2011press/eog-settlement.htm>
- Lutz, BD; Lewis, AN; Doyle, MW. (2013). Generation, transport, and disposal of wastewater associated with Marcellus Shale gas development. *Water Resour Res* 49: 647-656.

- Mantell, ME. (2011). Produced water reuse and recycling challenges and opportunities across major shale plays. Presentation presented at Hydraulic Fracturing Study: March 2011 Technical Workshop #4 on Water Resources Management, March 29-30, 2011, Arlington, VA.
- Mantell, ME. (2013b). Recycling and reuse of produced water to reduce freshwater use in hydraulic fracturing operations. In Summary of the technical workshop on water acquisition modeling: Assessing impacts through modeling and other means (pp. A20-A27). Washington, D.C.: U.S. Environmental Protection Agency. <http://www2.epa.gov/hfstudy/summary-technical-workshop-water-acquisition-modeling-assessing-impacts-through-modeling-and>
- Marshak, S. (2004). Essentials of geology (1st ed.). New York, NY: W.W. Norton and Company.
- McElreath, D. (2011). Comparison of hydraulic fracturing fluids composition with produced formation water following fracturing Implications for fate and transport. Presentation presented at Hydraulic Fracturing Study: March 2011 Technical Workshop on Fate and Transport, March 28-29, 2011, Arlington, VA.
- McIntosh, JC; Walter, LM. (2005). Volumetrically significant recharge of Pleistocene glacial meltwaters into epicratonic basins: Constraints imposed by solute mass balances. Chem Geol 222: 292-309. <http://dx.doi.org/10.1016/j.chemgeo.2005.07.010>
- McIntosh, JC; Walter, LM; Martini, AM. (2002). Pleistocene recharge to midcontinent basins: effects on salinity structure and microbial gas generation. Geochim Cosmochim Acta 66: 1681-1700. [http://dx.doi.org/10.1016/S0016-7037\(01\)00885-7](http://dx.doi.org/10.1016/S0016-7037(01)00885-7)
- Minnich, K. (2011). A water chemistry perspective on flowback reuse with several case studies. Minnich, K. http://www2.epa.gov/sites/production/files/documents/10_Minnich_-_Chemistry_508.pdf
- Montana GWIC (Montana Ground Water Information Center). (2009). Coal bed methane powder river basin: Montana Bureau of Mines and Geology Ground Water Information Center. Butte, MT.
- Mouser, P; Liu, S; Cluff, M; McHugh, M; Lenhart, J; MacRae, J. (In Press) Biodegradation of hydraulic fracturing fluid organic additives in sediment-groundwater microcosms.
- Murali Mohan, A; Hartsock, A; Hammack, RW; Vidic, RD; Gregory, KB. (2013). Microbial communities in flowback water impoundments from hydraulic fracturing for recovery of shale gas. FEMS Microbiol Ecol. <http://dx.doi.org/10.1111/1574-6941.12183>
- Neff, JM. (2002). Bioaccumulation in marine organisms: Effect of contaminants from oil well produced water. Amsterdam: Elsevier.
- Nelson, AW; May, D; Knight, AW; Eittrheim, ES; Mehrhoff, M; Shannon, R; Litman, R; Schultz, MK. (2014). Matrix complications in the determination of radium levels in hydraulic fracturing flowback water from Marcellus Shale. 1: 204-208. <http://dx.doi.org/10.1021/ez5000379>
- New Mexico Bureau of Mines and Mineral Resources. (1994). Coalbed methane in the upper cretaceous fruitland formation, San Juan Basin, New Mexico and Colorado. Socorro, NM: New Mexico Bureau of Mines and Mineral Resources, New Mexico Institute of Mining and Technology. <https://geoinfo.nmt.edu/publications/monographs/bulletins/146/>
- Nicot, JP; Scanlon, BR. (2012). Water use for shale-gas production in Texas, U.S. Environ Sci Technol 46: 3580-3586. <http://dx.doi.org/10.1021/es204602t>
- Nicot, JP; Scanlon, BR; Reedy, RC; Costley, RA. (2014). Source and fate of hydraulic fracturing water in the Barnett Shale: a historical perspective. Environ Sci Technol 48: 2464-2471. <http://dx.doi.org/10.1021/es404050r>
- North Dakota Department of Health. (2015). Oil field environmental incident summary, incident 20150107160242. Available online at http://www.ndhealth.gov/EHS/FOIA/Spills/Summary_Reports/20150107160242_Summary_Report.pdf

- NRC (National Research Council). (2010). Management and effects of coalbed methane produced water in the western United States. Washington, DC: National Academies Press.
http://www.nap.edu/catalog.php?record_id=12915
- NSTC (National Science and Technology Council). (2000). Integrated assessment of hypoxia in the Northern Gulf of Mexico. Washington, DC: U.S. National Science and Technology Council, Committee on Environment and Natural Resources. http://oceanservice.noaa.gov/products/hypox_final.pdf
- Olawoyin, R; Wang, JY; Oyewole, SA. (2013). Environmental safety assessment of drilling operations in the Marcellus-shale gas development. S P E Drilling & Completion 28: 212-220.
<http://dx.doi.org/10.2118/163095-PA>
- Olmstead, SM; Muehlenbachs, LA; Shih, JS; Chu, Z; Krupnick, AJ. (2013). Shale gas development impacts on surface water quality in Pennsylvania. PNAS 110: 4962-4967.
<http://dx.doi.org/10.1073/pnas.1213871110>
- Orem, W; Tatu, C; Varonka, M; Lerch, H; Bates, A; Engle, M; Crosby, L; McIntosh, I. (2014). Organic substances in produced and formation water from unconventional natural gas extraction in coal and shale. Int J Coal Geol 126: 20-31. <http://dx.doi.org/10.1016/j.coal.2014.01.003>
- Orem, WH; Tatu, CA; Lerch, HE; Rice, CA; Bartos, TT; Bates, AL; Tewalt, S; Corum, MD. (2007). Organic compounds in produced waters from coalbed natural gas wells in the Powder River Basin, Wyoming, USA. Appl Geochem 22: 2240-2256. <http://dx.doi.org/10.1016/j.apgeochem.2007.04.010>
- Ottom, JK; Zielinski, RA; Smith, BD; Abbott, MM. (2007). Geologic controls on movement of produced-water releases at US geological survey research Site A, Skiatook lake, Osage county, Oklahoma. Appl Geochem 22: 2138-2154. <http://dx.doi.org/10.1016/j.apgeochem.2007.04.015>
- PA DCNR (Pennsylvania Department of Conservation and Natural Resources). (2015). Thermal maturation and petroleum generation. Available online at http://www.dcnr.state.pa.us/topogeo/econresource/oilandgas/marcellus/sourcerock_index/sourcerock_maturation/index.htm (accessed April 9, 2015).
- PA DEP (Pennsylvania Department of Environmental Protection). (2009a). Inspection Report, inspection record #1835041, enforcement record #251134. Harrisburg, PA: Commonwealth of Pennsylvania Department of Environmental Protection, Oil and Gas Management Program.
- PA DEP (Pennsylvania Department of Environmental Protection). (2010). DEP Fines Atlas Resources for drilling wastewater spill in Washington County. Available online at <http://www.portal.state.pa.us/portal/server.pt/community/newsroom/14287?id=13595&typeid=1> (accessed February 13, 2014).
- PA DEP (Pennsylvania Department of Environmental Protection). (2011c). Surface water sample analytical results from XTO 308 response data from XTO February 3, 2011 CAWP addendum. Indiana, PA: XTO Energy.
- PA DEP (Pennsylvania Department of Environmental Protection). (2015b). Technologically enhanced naturally occurring radioactive materials (TENORM) study report. Harrisburg, PA.
<http://www.eLibrary.dep.state.pa.us/dsweb/Get/Document-105822/PA-DEP-TENORM-Study-Report-Rev.0-01-15-2015.pdf>
- Papoulias, DM; Velasco, AL. (2013). Histopathological analysis of fish from Acorn Fork Creek, Kentucky, exposed to hydraulic fracturing fluid releases. Southeastern Naturalist 12: 92-111.
- Pattera, P. (2011). DEP shuts down Tri-County Waste Water over illegal dumping. Available online at http://triblive.com/x/pittsburghtrib/news/regional/s_728516.html#axzz3UCvkvM7t (accessed March 12, 2015).
- Peterman, ZE; Thamke, J; Futa, K; Oliver, T. (2012). Strontium isotope evolution of produced water in the East Poplar Oil Field, Montana. Presentation presented at US Geological Survey AAPG annual convention and exhibition, April 23, 2012, Long Beach, California.

- Repetski, JE; Ryder, RT; Weary, DJ; Harris, AG; Trippie, MH. (2008). Thermal maturity patterns (CAI and %Ro) in upper ordovician and devonian rocks of the Appalachian Basin: A major revision of USGS map I917E using new subsurface collections. U.S. Geological Survey. <http://pubs.usgs.gov/sim/3006/SIM3006.pdf>
- Reuters. (2014). UPDATE 2-oil well in North Dakota out of control, leaking. Available online at <http://www.reuters.com/article/2014/02/14/energy-crude-blowout-idUSL2N0LJ15820140214> (accessed March 2, 2015).
- Reynolds, RR; Kiker, RD. (2003). Produced water and associated issues a manual for the independent operator. (Oklahoma Geological Survey Open-File Report 6-2003). Tulsa, OK: Oklahoma Geological Survey. http://karl.nrcce.wvu.edu/regional/pww/produced_water.pdf
- Rice, CA. (1999). Waters co-produced with coal-bed methane from the Ferron Sandstone in east central Utah: chemical and isotopic composition, volumes, and impacts of disposal [Abstract]. Geological Society of America Abstracts with Programs 31: A385.
- Rice, CA; Ellis, MS; Bullock, JH. (2000). Water co-produced with coalbed methane in the Powder River basin, Wyoming: Preliminary compositional data. (Open File-Report 00-372). Denver, CO: U.S. Department of the Interior, U.S. Geological Survey.
- Richter, BC; Kreitler, CW. (1993). Geochemical techniques for identifying sources of ground-water salinization. Boca Raton, FL: CRC Press. <http://www.crcpress.com/product/isbn/9781566700009>
- Rowan, EL; Engle, MA; Kirby, CS; Kraemer, TF. (2011). Radium content of oil- and gas-field produced waters in the northern Appalachian Basin (USA): Summary and discussion of data. (Scientific Investigations Report 20115135). Reston, VA: U.S. Geological Survey. <http://pubs.usgs.gov/sir/2011/5135/>
- Rowan, EL; Engle, MA; Kraemer, TF; Schroeder, KT; Hammack, RW; Doughten, MW. (2015). Geochemical and isotopic evolution of water produced from Middle Devonian Marcellus shale gas wells, Appalachian basin, Pennsylvania. AAPG Bulletin 99: 181-206. <http://dx.doi.org/10.1306/07071413146>
- Rozell, DJ; Reaven, SJ. (2012). Water pollution risk associated with natural gas extraction from the Marcellus Shale. Risk Anal 32: 13821393. <http://dx.doi.org/10.1111/j.1539-6924.2011.01757.x>
- Rushing, JA; Newsham, KE; Blasingame, TA. (2013). Rock typing: Keys to understanding productivity in tight gas sands. SPE Unconventional Reservoirs Conference, February 10-12, 2008, Keystone, Colorado, USA.
- SAIC and GES (SAIC Energy, Environment & Infrastructure, LLC and Groundwater & Environmental Services, Inc). (2011). ATGAS investigation initial site characterization and response, April 19, 2011 to May 2, 2011, ATGAS2H Well Pad, permit no. 37-015-21237, Leroy Township, Bradford County, PA. Harrisburg, Pennsylvania: Chesapeake Appalachia, LLC. http://www.chk.com/news/articles/documents/atgas_initial_site_characterization_report_final_08292011.pdf
- Sang, W; Stoof, CR; Zhang, W; Morales, VL; Gao, B; Kay, RW; Liu, L; Zhang, Y; Steenhuis, TS. (2014). Effect of hydrofracking fluid on colloid transport in the unsaturated zone. Environ Sci Technol 48: 8266-8274. <http://dx.doi.org/10.1021/es501441e>
- Schlegel, ME; McIntosh, JC; Petsch, ST; Orem, WH; Jones, EJP; Martini, AM. (2013). Extent and limits of biodegradation by in situ methanogenic consortia in shale and formation fluids. Appl Geochem 28: 172-184. <http://dx.doi.org/10.1016/j.apgeochem.2012.10.008>
- Schlumberger (Schlumberger Limited). (2014). Schlumberger oilfield glossary. Available online at <http://www.glossary.oilfield.slb.com/>
- Schmidley, EB; Smith, BJ. (2011). Personal communication from Schmidley and Smith to DiCello: CAWP Addendum EM Survey & Well Location; XTO Energy, Inc. Marquardt Release. Available online

- [Schmidt, V; McDonald, DA.](#) (1979). The role of secondary porosity in the course of sandstone diagenesis. In PA Schole; PR Schluger (Eds.), Aspects of diagenesis : based on symposia sponsored by the Eastern and by the Rocky Mountain Sections, The Society of Economic Paleontologists and Mineralogists (pp. 175-207). Tulsa, OK: The Society of Economic Paleontologists and Mineralogists (SEPM).
http://archives.datapages.com/data/sepm_sp/SP26/The_Role_of_Secondary_Porosity.html
- [Schwarzenbach, RP; Gschwend, PM; Imboden, DM.](#) (2002). Environmental Organic Chemistry. In Environmental organic chemistry (2 ed.). Hoboken, NJ: John Wiley & Sons, Inc.
- [Science Applications International Corporation.](#) (2010). XTO - Marquardt pad soil and water corrective action workplan. (XTO-EPA0001074). Indiana, PA: XTO Energy.
- [Šimuněk, J; Šejna, M; van Genuchten, MT.](#) (1998). The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably-saturated media, Version 2.0, IGWMC-TPS-70. Available online
- [Sirivedhin, T; Dallbauman, L.](#) (2004). Organic matrix in produced water from the Osage-Skiatook petroleum environmental research site, Osage county, Oklahoma. Chemosphere 57: 463-469.
- [States, S; Cyprych, G; Stoner, M; Wydra, F; Kuchta, J; Monnell, J; Casson, L.](#) (2013). Marcellus Shale drilling and brominated THMs in Pittsburgh, Pa., drinking water. J Am Water Works Assoc 105: E432-E448.
<http://dx.doi.org/10.5942/jawwa.2013.105.0093>
- [Stewart, DR.](#) (2013a). Analytical testing for hydraulic fracturing fluid water recovery and reuse. In Summary of the technical workshop on analytical chemical methods (pp. B6-B10). Stewart, DR.
<http://www2.epa.gov/sites/production/files/documents/analytical-chemical-methods-technical-workshop-summary.pdf>
- [Strong, L; Gould, T; Kasinkas, L; Sadowsky, M; Aksan, A; Wackett, L.](#) (2013). Biodegradation in waters from hydraulic fracturing: chemistry, microbiology, and engineering. J Environ Eng 140: B4013001.
[http://dx.doi.org/10.1061/\(ASCE\)EE.1943-7870.0000792](http://dx.doi.org/10.1061/(ASCE)EE.1943-7870.0000792)
- [Sturchio, NC; Banner, JL; Binz, CM; Heraty, LB; Musgrove, M.](#) (2001). Radium geochemistry of ground waters in Paleozoic carbonate aquifers, midcontinent, USA. Appl Geochem 16: 109-122.
- [Sumi, L.](#) (2004). Pit pollution: Backgrounder on the issues, with a New Mexico case study. Washington, DC: Earthworks: Oil and Gas Accountability Project.
<http://www.earthworksaction.org/files/publications/PitReport.pdf>
- [Sun, M; Lowry, GV; Gregory, KB.](#) (2013). Selective oxidation of bromide in wastewater brines from hydraulic fracturing. Water Res 47: 3723-3731. <http://dx.doi.org/10.1016/j.watres.2013.04.041>
- [Swanson, VE.](#) (1955). Uranium in marine black shales of the United States. In Contributions to the geology of uranium and thorium by the United States Geological Survey and Atomic Energy Commission for the United Nations International Conference on Peaceful Uses of Atomic Energy, Geneva, Switzerland, 1955 (pp. 451-456). Reston, VA: U.S. Geological Survey. <http://pubs.usgs.gov/pp/0300/report.pdf>
- [Thordsen, JJ; . Kharaka, YK; Ambats, G; Kakouros, E; Abbott, MM.](#) (2007). Geochemical data from produced water contamination investigations: Osage-Skiatook Petroleum Environmental Research (OSPER) sites, Osage County, Oklahoma. (Open-File Report 2007-1055). Reston, VA: United States Geological Survey.
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (1992). Guidance for data useability in risk assessment (part A) - final. (Publication 9285.7-09A). Washington, D.C.
<http://www.epa.gov/oswer/riskassessment/datause/parta.htm>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (1999). Understanding oil spills and oil spill response [EPA Report]. (EPA 540-K-99-007). Washington, D.C.: U.S. Environmental Protection Agency, Office of Emergency and Remedial Response.
<http://www4.nau.edu/itep/waste/hazsubmap/docs/OilSpill/EPAUnderstandingOilSpillsAndOilSpillResponse1999.pdf>

- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2004). Evaluation of impacts to underground sources of drinking water by hydraulic fracturing of coalbed methane reservoirs. (EPA/816/R-04/003). Washington, DC.: U.S. Environmental Protection Agency, Office of Solid Waste.
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2007). Monitored natural attenuation of inorganic contaminants in ground water: volume 1 technical basis for assessment [EPA Report]. (EPA/600/R-07/139). Washington, D.C. <http://nepis.epa.gov/Adobe/PDF/60000N4K.pdf>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2012a). 5.2 Dissolved oxygen and biochemical oxygen demand. In Water Monitoring and Assessment. <http://water.epa.gov/type/rsl/monitoring/vms52.cfm>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2012f). Study of the potential impacts of hydraulic fracturing on drinking water resources: Progress report. (EPA/601/R-12/011). Washington, DC: U.S. Environmental Protection Agency, Office of Research and Development. <http://nepis.epa.gov/exe/ZyPURL.cgi?Dockkey=P100FH8M.txt>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2013e). SW-846 on-line. Available online at <http://www.epa.gov/epawaste/hazard/testmethods/sw846/online/index.htm> (accessed April 8, 2015).
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2013g). XTO Energy, Inc. Settlement. Available online at <http://www2.epa.gov/enforcement/xto-energy-inc-settlement>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2014b). Development of rapid radiochemical method for gross alpha and gross beta activity concentration in flowback and produced waters from hydraulic fracturing operations [EPA Report]. (EPA/600/R-14/107). Washington, D.C. <http://www2.epa.gov/hfstudy/development-rapid-radiochemical-method-gross-alpha-and-gross-beta-activity-concentration>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2014b). The verification of a method for detecting and quantifying diethylene glycol, triethylene glycol, tetraethylene glycol, 2-butoxyethanol and 2-methoxyethanol in ground and surface waters [EPA Report]. (EPA/600/R-14/008). Washington, D.C. <http://www2.epa.gov/hfstudy/verification-method-detecting-and-quantifying-diethylene-glycol-triethylene-glycol>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2015j). Retrospective case study in Killdeer, North Dakota: study of the potential impacts of hydraulic fracturing on drinking water resources [EPA Report]. (EPA 600/R-14/103). Washington, D.C.
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2015k). Retrospective case study in southwestern Pennsylvania: study of the potential impacts of hydraulic fracturing on drinking water resources [EPA Report]. (EPA 600/R-14/084). Washington, D.C.
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2015m). Retrospective case study in Wise County, Texas: study of the potential impacts of hydraulic fracturing on drinking water resources [EPA Report]. (EPA 600/R-14/090). Washington, D.C.
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2015n). Review of state and industry spill data: characterization of hydraulic fracturing-related spills [EPA Report]. (EPA/601/R-14/001). Washington, D.C.: Office of Research and Development, U.S. Environmental Protection Agency.
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2015q). Technical development document for proposed effluent limitation guidelines and standards for oil and gas extraction. (EPA-821-R-15-003). Washington, D.C. <http://water.epa.gov/scitech/wastetech/guide/oilandgas/unconv.cfm>
- [U.S. GAO](#) (U.S. Government Accountability Office). (2012). Energy-water nexus: Information on the quantity, quality, and management of water produced during oil and gas production. (GAO-12-156). Washington, D.C. <http://www.gao.gov/products/GAO-12-156>

- USGS (U.S. Geological Survey). (2006). Produced Water Database [Database]: U.S. Geological Survey :: USGS. Retrieved from <http://energy.usgs.gov/EnvironmentalAspects/EnvironmentalAspectsofEnergyProductionandUse/ProducedWaters.aspx#3822110-overview>
- USGS (U.S. Geological Survey). (2010). Volatile organic compounds in the nation's ground water and drinking-water supply wells: Supporting information. Glossary. Available online at http://water.usgs.gov/nawqa/vocs/national_assessment/report/glossary.html
- USGS (U.S. Geological Survey). (2013b). National hydrography dataset: High-resolution flowline data: The national map. Retrieved from <http://viewer.nationalmap.gov/viewer/>
- USGS (U.S. Geological Survey). (2014f). USGS investigations of water produced during hydrocarbon reservoir development [Fact Sheet]. Reston, VA. <http://dx.doi.org/10.3133/fs20143104>
- Vaidyanathan, G. (2013a). Hydraulic fracturing: when 2 wells meet, spills can often follow. Available online at <http://www.eenews.net/energywire/stories/1059985587> (accessed September 2, 2014).
- Vaidyanathan, G. (2013b). XTO comes out swinging against 'unwarranted' criminal charges in Pa. E&E News 0.
- Van Voast, WA. (2003). Geochemical signature of formation waters associated with coalbed methane. AAPG Bulletin 87: 667-676.
- Vengosh, A; Jackson, RB; Warner, N; Darrah, TH; Kondash, A. (2014). A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States. Environ Sci Technol 48: 36-52. <http://dx.doi.org/10.1021/es405118y>
- Vidic, RD; Brantley, SL; Vandenbossche, JM; Yoxtheimer, D; Abad, JD. (2013). Impact of shale gas development on regional water quality [Review]. Science 340: 1235009. <http://dx.doi.org/10.1126/science.1235009>
- Vine, JD; Tourtelot, EB. (1970). Geochemistry of black shale deposits; A summary report. Econ Geol 65: 253-272. <http://dx.doi.org/10.2113/gsecongeo.65.3.253>
- Vittitow, JG, Sr. (2010). Well control incident analysis, EOG Resources Inc., Punxautawney Hunting Club 36H, Clearfield County, Pennsylvania. Bedrock Engineering. http://www.pahouse.com/EnvResources/documents/BEDROCK_ENGINEERING_PHC_36H_Incident_Report_Final.pdf
- Warner, NR; Kresse, TM; Hays, PD; Down, A; Karr, JD; Jackson, RB; Vengosh, A. (2013b). Geochemical and isotopic variations in shallow groundwater in areas of the Fayetteville Shale development, north-central Arkansas. Appl Geochem 35: 207-220.
- Whittemore, DO. (2007). Fate and identification of oil-brine contamination in different hydrogeologic settings. Appl Geochem 22: 2099-2114. <http://dx.doi.org/10.1016/j.apgeochem.2007.04.002>
- Williams, JE; Taylor, LE; Low, DJ. (1998). Hydrogeology and Groundwater Quality of the Glaciated Valleys of Bradford, Tioga, and Potter Counties, Pennsylvania. 98.
- Wilson, B. (2014). Geologic and baseline groundwater evidence for naturally occurring, shallowly sourced, thermogenic gas in northeastern Pennsylvania. AAPG Bulletin 98: 373-394. <http://dx.doi.org/10.1306/08061312218>
- Wuchter, C; Banning, E; Mincer, TJ; Drenzek, NJ; Coolen, MJ. (2013). Microbial diversity and methanogenic activity of Antrim Shale formation waters from recently fractured wells. FMICB 4: 1-14. <http://dx.doi.org/10.3389/fmicb.2013.00367>
- Xu, B; Hill, AD; Zhu, D; Wang, L. (2011). Experimental evaluation of guar fracture fluid filter cake behavior. Paper presented at SPE Hydraulic Fracturing Technology Conference, January 24-26, 2011, The Woodlands, TX.

[Ziemkiewicz, P; Quaranta, JD; Mccawley, M.](#) (2014). Practical measures for reducing the risk of environmental contamination in shale energy production. Environ Sci Process Impacts 16: 1692-1699.
<http://dx.doi.org/10.1039/c3em00510k>